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# Intercomparison exercise for heavy metals in $PM_{10}$

M. Gerboles and D. Buzica

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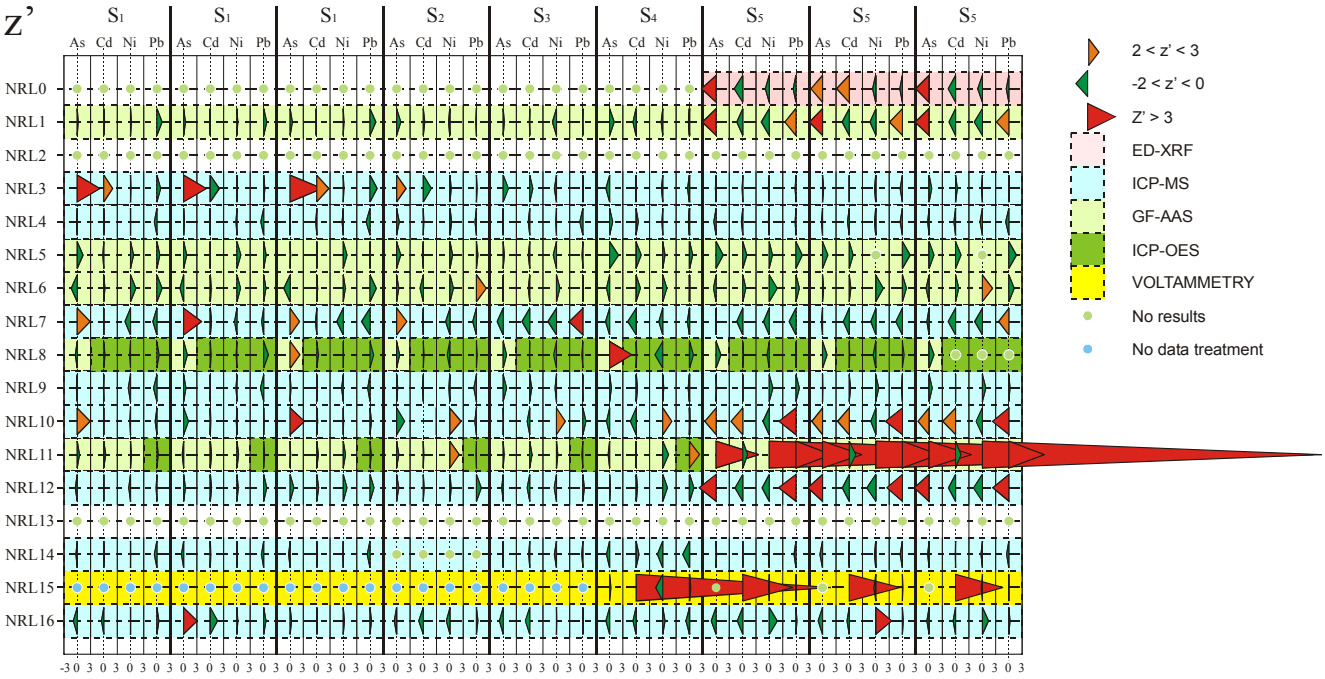


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# Summary

The Joint Research Centre (JRC) has carried out an Intercomparison Exercise (IE) for the determination of heavy metals in particulate matter ($PM_{10}$). The IE focussed on lead (Pb), arsenic (As), nickel (Ni) and cadmium (Cd), the heavy metals regulated by the 1st and 4th Daughter Directives for Air Pollution. Copper (Cu), chromium (Cr) and zinc (Zn), the elements included in the EMEP programme together with aluminium (Al), cobalt (Co), iron (Fe), manganese (Mn) and vanadium (V) were also tested. Fourteen laboratories, generally members of the Network of Air Quality Reference Laboratories (AQUILA), participated in the IE. The participants mainly used microwave digestion with nitric acid and hydrogen peroxide and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) for analysis as recommended in the reference method (EN 14902). However, a few participants used other methods: Energy Dispersive X-ray Fluorescence (EDXRF), Optical Emission Spectrometry (ICP-OES) and Voltammetry for analysis while digestion was performed by vaporisation on hot plate before microwave digestion, Soxhlet extraction, high pressure or cold hydrogen fluoride methods.

Each participant received 5 samples to be analysed: (1) a liquid sample prepared by dilution of a Certified Reference Material (CRM), (2) a solution of a dust CRM sample digested by the JRC, (3) a sub-sample of a dust CRM that each participating laboratory had to digest and analyse, (4) a solution prepared by JRC after digestion of an exposed filter and (5) a pair of filters (one blank filter and one exposed filter) to be digested and analysed by each participant.

For 89 % of all types of samples, the Data Quality Objectives (DQOs) of the 1st and 4th European Directives (uncertainty of 25 % for Pb and 40 % for As, Cd and Ni) were met. All together, this is a good score. The best results were obtained for the liquid CRM, dust CRM digested by JRC, dust CRM and filter digested by JRC with 92, 90, 96 and 93 % of DQOs being met, respectively. It was found that the DQOs were not met if the difference of acidity between test samples and participant calibration standards was high.

Conversely, only 76 % of DQOs were met for the filter to be digested by each participant with about 85 % for Cd and Ni, 73% for Pb and 64 % for As, the latter element being the most difficult to determine. The worst results were associated with special events: explosion due to overpressure in microwave oven during digestion for two participants, a wrong dilution factor used by one participant and a huge contamination in the blank filter for another participant. Among the two explosions, one of them was probably the effect of a lack of temperature control in the digestion vessel. For the other explosion, the microwave digestion and the digestion program advised by EN 14902 is to be questioned. Moreover, satisfactory results were obtained using Soxhlet extraction, high pressure method and cold hydrogen fluoride digestion methods which are not presented in EN 14902. The DQOs of As and Cd could not be met with EDXRF whose limit of detection was too high for these two elements and for Cd using Voltammetry which suffered a strong interference for this element.

Regarding the methods of analysis, apart from the points mentioned above about EDXRF and Voltammetry, good results were observed using ICP-OES for Cd, Ni and Pb. A few discrepancies were also registered for GF-AAS and ICP-MS but they were created by the special events or acidity problem mentioned above. This shows that even though GF-AAS and ICP-MS are found suitable, the implementation by each participant may be responsible for important mistakes.

The results of the IE showed that for 77 % of analysis, the uncertainty of measurements estimated by participants was consistent with the differences between the participant results and the reference values of the test samples. In average, participants claimed uncertainties that were consistent with the DQOs: about 10 % for Pb and between 15 and 20 % for As, Cd and Ni. The discrepancies were mainly produced either by some participants underestimating their uncertainty of measurements or by the explosions, wrong dilution factor, contamination, high limit of detection, interference mentioned before.

Once these special events are discarded, the reproducibility for all samples and participants show values between 41 and 54 %. These figures are consistent with the DQOs if one takes into consideration that reproducibility should be compared to √2 of the DQOs. The repeatability remains between 5 and 12 % without much difference according to the sample type. Only the analysis of As on filter gives higher repeatability of up to 20 %. The reproducibility was higher than the repeatability. Furthermore, for a majority of participants the between day variability, determined on three different days with different calibration, was higher than the within-day variability of measurements. These two observations suggest that it should be still possible to improve the quality of measurements by implementing more stringent procedures of quality control.

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## Abbreviations

AQUILA: Network of Air Quality Reference Laboratories
CAFÉ: European Directive for Ambient Air Quality and Cleaner Air for Europe
CEN: Comité Européen de Normalisation
CRM : Certified Reference Material
DQO : Data Quality Objective
EDXRF: Energy Dispersive X-ray Fluorescence
GF-AAS: Graphite Furnace Atomic Absorption Spectrometry
ICP-AES or ICP-OES: Atomic Emission Spectrometry or Optical Emission Spectrometry
ICP-MS: Inductively Coupled Plasma Mass Spectrometry
IEs: Intercomparison exercises
ISO: International Standard Organisation
JRC: Joint Research Centre
LVS: Low Volume Sampler
NIST: National Institute of Standards and Technology
NRLs: National Reference Laboratories
PFA: Perfluoroalkoxy copolymer
PM: Particulate Matter
PIXE: Proton Induced X-ray Emission
RSD: Relative Standard Deviation

# Symbols

En: normalized deviation,
r: repeatability,
R: reproducibility,
x : NRLs' value,
X: reference/assigned value,
$\sigma_p$: fitness-for-purpose-based standard deviation for proficiency assessment,
$u_X$: standard uncertainty of the reference/assigned value,
$u_s$: standard uncertainty of sampling,
$u_e$: standard uncertainty of digestion,
$u_m$: standard uncertainty of interference/matrix effects,
$\sigma_{p,r}$: relative fitness-for-purpose-based standard deviation,
$u_{s,r}$: relative standard uncertainty of sampling,
$u_{e,r}$: relative standard uncertainty of digestion,
$u_{m,r}$: relative standard uncertainty of interference/matrix effects,
$U_x$: expanded uncertainty,
$U_{x,r}$: relative expanded uncertainty of measurements claimed by NRLs for their results
$U_X$: expanded uncertainty of the reference/assigned value of test samples $S_1$ to $S_5$.
$C_{BY14}$ and $C_{R14}$: certified heavy metals concentrations given for ROMIL BY14 and R14,
$V_{BY14}$ and $V_{R14}$: volumes of the CRMs ROMIL BY14 and R14 used to prepare $S_1$,
$m_{0.1}$ and $m_{0.9}$ : the masses of water used to determine $V_{BY14}$ and $V_{R14}$,
$d_{water}$: the density of water, gravimetrically determined, used to determine $V_{BY14}$ and $V_{R14}$,
Blk: trace of heavy metals in the MilliQ water, $HNO_3$ and in the different glass/PFA vessels used to prepare $S_1$,
$d_{BY14}$ and $d_{R14}$: the densities of the CRMs ROMIL BY14 and R14,
m: weighted mass of NIST SRM 1648 used to prepare test samples $S_2$ and $S_3$,
CRM: certified heavy metal mass ratios of the NIST SRM 1648,
V: final volume of test sample $S_2$,
k: efficiency of digestion performed by JRC of the NIST 1648 sub-sample for preparing $S_2$,
$m_{HM}$: masses of heavy metal determined by each NRL for $S_3$.
s*: the robust standard deviation of the assigned values of $S_4$ and $S_5$,
p: number of laboratories used to determine the assigned values of $S_4$ and $S_5$.

# Introduction and objectives

Since the adoption of the framework directive 96/62/EC[1] on ambient air quality assessment and management, the European Commission (EC) has intensively worked on the implementation of a harmonized programme for the monitoring of air pollution in Europe. With the goal of improving the quality of the measurements, stricter protocols for a series of items like definition of sampling criteria, zones, locations and data quality objectives (DQOs) have been defined. Reference methods were stated by the Commission and successively standardised by the Comité Européen de Normalisation (CEN). The improvement of reference materials, primary standards, traceability and the definition of equivalent methods are of greater interest in the EU ambient air policy programme. Furthermore, emphasis has been placed on the implementation of an operative structure that can guarantee the data quality from the local network to regional, national and European level through traceability chains. Member States were invited to nominate National Reference Laboratories (NRLs) responsible for the evaluation and approval of instrumentation, the quality assurance and quality control (QA/QC) of air pollution measurements, the coordination at national level of the measurement strategy and the collaboration at European level with the Commission through the Network of Air Quality Reference Laboratories (AQUILA). All these points have been gathered and reviewed under the recent Directive Proposal on Ambient Air Quality and Cleaner Air for Europe (the "CAFE" Directive)[2] (COM(2005) 447).

Since the beginning of the 90's, the Joint Research Centre (JRC) organizes laboratory intercomparison exercises (IEs). These IEs aim at checking the accuracy of measurements of NRLs with regards to the DQOs given in the Directives and improving the comparability of air pollution monitoring techniques. Accredited NRLs use these IEs to demonstrate proficiency as requested by ISO 17025[3]. The IEs started with the measurement of nitrogen dioxide ($NO_2$) and ozone ($O_3$) in dry air[4,5]. Finally, a routine programme has been established in which NRLs are invited every 3 years to participate in the IEs which either takes place in Ispra (I) at the JRC or in Essen (LANUV-G). They consist of 1-week laboratory exercises for $NO_2$, NO, NOx, CO, $SO_2$ and $O_3$[6]. The trend of the IEs'results shows an improvement of data quality since the early 90's especially observed with NRLs accredited according to ISO 17025. During the latest IEs for inorganic gases, the effect of interference due to water vapour and organic gaseous compounds has been also studied. JRC has organized several IEs for organic pollutants either as round robins in canisters/cylinders or with dynamic dilution of synthetic mixtures generated in a laboratory calibration bench. In 2006, the 1st IE for Benzene, Toluene, Ethyl-benzene & *m,p,o*-Xylenes (BTEX) took place at the JRC. It was intended to provide information on the state of compliance with DQO and on the major sources of uncertainty for BTEX measurements with automatic analyzers (i.e. linearity, memory effects, humidity effects, ozone effects and volatile organic compounds interference effects)[7]. A round robin for poly aromatic hydrocarbons was launched in 2007. JRC also performed field intercomparison exercises with mobile laboratories as QA/QC of routine measurements of automatic monitoring stations e. g. the field programme for $O_3$, NO, $NO_2$, and $SO_2$[8]. JRC is currently running a field IE for particulate matter ($PM_{10}$) to provide further information

1 Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management

2 Proposal for a Directive of the European Parliament and of the Council on ambient air quality and Cleaner Air for Europe, COM (2005) 447 (21.09.2005)

3 International standards, ISO/IEC 17025:2005, General requirements for the competence of testing and calibration laboratories, Geneva (CH)

4 European Comparison of nitrogen dioxide calibration methods quality assurance programme n°1, QAP/1 of the European directive for nitrogen dioxide, EUR 17661 EN, (1997). E. de Saeger, M. Gerboles, H. Rau, M. Payrissat,

5 E. de Saeger, A. Noriega Guerra, P. Perez Ballesta, M. Gerboles, H. Rau, L. Amantini, M. Payrissat, Harmonization of Directive 92/72 on Air Pollution by Ozone.- Intercomparison of Calibration Procedures for Ozone Measurements, EUR Report 17662 EN (1997).

6 EC Harmonisation Programme for Air Quality Measurements. Intercomparison Exercises 1999/2000 for SO2, CO, NO2 and O3, EUR 19629 EN, 2000. Borowiak, A., Lagler, F., Gerboles, M., De Saeger, E.,

7 P. Perez Ballesta, R. Field, E. de Saeger, Interlaboratory exercises for volatile organic compounds determination, Atmospheric Environment 2001, 35, 5729–5740, and P. Perez Ballesta, R. A. Field, R. Connolly, F. Lagler, I. Nikolova and N. Cao, First EC-JRC aromatic (BTEX) compounds intercomparison with automatic analyzers, EUR 22523 EN, 2006.

8 Payrissat,M., Gerboles, M., Sieja, B., de Saeger, E., Quality Assessment of Ambient NO, NO2 and SO2 Measurements in European Monitoring Networks, European Commission, 1997, EUR Report 17671 EN

on the comparability of $PM_{10}$ measurements carried out by the NRLs of AQUILA and of correction factors for automatic $PM_{10}$-monitors.

For the so-called indicative methods included in the Framework Directive, JRC also carried out several IEs for diffusive samplers[9]. These IEs aimed at evaluating the extent of differences between measurements performed using $O_3$ and $NO_2$ diffusive samplers and by the reference methods. The tests were performed under laboratory and field conditions. Furthermore, JRC carried out a proficiency testing for network laboratories using $NO_2$ diffusive samplers[10].

In 2006, JRC proposed to launch an IE for the determination of heavy metals in particulate matter ($PM_{10}$). The purpose of this IE was to inform the Directorate General for Environment (DG-ENV) of the European Commission and other stakeholders about the state of comparability and uncertainty in heavy metals determinations achieved by NRLs. The IE was focussed on the measurement of the heavy metals regulated by the 1st and 4th Daughter Directives (1999/30/EC[11] and 2004/107/EC[12]): lead (Pb), arsenic (As), nickel (Ni) and cadmium (Cd). The design of the experiment and the data treatment aimed at meeting the following objectives:

1. To assess whether the DQO of the European Directives 1999/30/EC and 2004/107/EC relating to lead, arsenic, cadmium and nickel are met;
2. To assess if the uncertainty reported by NRLs are confirmed by the difference between their results and the reference values of the test samples (proficiency test for accredited laboratories);
3. To evaluate the repeatability/reproducibility of the method of measurements for each heavy metal and for each type of sample; to evaluate the repeatability/reproducibility of each laboratory;
4. To identify the main sources of uncertainty and analytical deviations: e. g. calibration, digestion, analysis and matrix effect. This could help the definition of possible investigatory and/or remedial actions;

This EUR report presents the results of the intercomparison exercise. Blind results are given.

# Participants, analytical methods and test samples

All the members of the AQUILA network were invited to participate in this IE. Table 1 shows the NRLs which registered for participating in this IE. Table 3 gives the method of digestion and analysis, the origin of the traceability of standards used for calibration, the status of accreditation and the method of estimation of uncertainty of measurements for each participant. Two laboratories (RIVM-NL and NERI –Denmark) had to withdraw as they were not able to deliver results in time. The Polish laboratory, Chief Inspectorate of Environmental Protection, was not the National Reference Laboratory of Poland but a regional laboratory.

The 4th Daughter Directive stated that for the determination of heavy metals in $PM_{10}$ either Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) shall be used as reference methods. However among the participants of this IE, NRL 0 used Energy Dispersive X-ray Fluorescence (EDXRF), NRL 3 planned to use Proton Induced X-ray Emission (PIXE), NRL 8 and 11 used Optical Emission Spectrometry (ICP-OES) and NRL 15 used Voltammetry. The equivalence of these methods to the reference methods according to the EC

9 M. Gerboles, D. Buzica, L. Amantini and F. Lager, Laboratory and field comparison of measurements obtained using the available diffusive samplers for ozone and nitrogen dioxide in ambient air, J. Environ. Monit., 2006, 8, 112–119.

10 M. Gerboles, D. Buzica, L. Amantini, Intercomparison exercises for the monitoring of ambient nitrogen dioxide using diffusive samplers, Pollution Atmospherique, 2004, 183, 345-359.

11 Council Directive 1999/30/EC of 22 April 1999 relating to limit values for sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter and lead in ambient air, [Official Journal L 163 of 29.06.1999]

12 Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air. Official Journal L 023 , 26/01/2005 P. 0003 - 0016

protocol[13] has not been demonstrated yet. However, it was decided to accept any measuring methods implemented by a NRL so that the IE would be able to catch the whole picture of the data quality for heavy metals monitoring in the EU.

**Table 1: National Reference Laboratories participating in the intercomparison exercise.**

| Country | | NRLs | Contact persons |
|---|---|---|---|
| Belgium | VMM | Flemish Environment Agency (VMM) | E. Adriaenssens, N. Claeys |
| The Netherlands | RIVM | National Institute for Public Health and the Environment (RIVM) | S. Piso, B. Artman |
| Austria | UBA | Umweltbundesamt GmbH (UBA) | A. Hanus-Illnar, M. Salfinger |
| France | EMD | Ecole des Mines de Douai (EMD) | L. Alleman |
| Croatia | IMI | Institute for Medical Research and Occupational Health, | K. Sega |
| Lithuania | EPA | Environmental Protection Agency (EPA) | D. Pockeviciute |
| Czech Republic | CZMI | Czech Hydrometeorological Institute (CMHI) | S. Rychlik , E. Rabinak, J Novak |
| Germany | LANUV | NRW State Agency for Nature, Environment, and Consumer Protection | U. Pfeffer, D. Gladtke, A. Olschewski |
| Slovenia | ARSO | Environmental Agency of the Republic of Slovenia | J. Tursic |
| Ireland, | EPA | Environmental Protection Agency | B. O'Leary |
| Poland | GIOS | Chief Inspectorate of Environmental Protection | J. Biel-Cwikowska |
| Finland | FMI | Finnish Meteorological Institute | V. Karlsson |
| Denmark | NERI | National Environmental Research Institute | C. Monies |
| United Kingdom | NPL | National Physical Laboratory, Analytical Science, Quality of Life Division | R. Yardley |
| EC | JRC | JRC – Institute for Environment and Sustainability | D. Buzica, M. Gerboles, G. Tanet, R. Passarella, V. Pedroni |

Initially, it was planned to test only the heavy metals in $PM_{10}$ regulated by the European Directives: Pb, As, Ni and Cd. NRLs proposed to extend the IE to other sensitive heavy metals: first, the ones included in the EMEP programme: copper (Cu), chromium (Cr) and zinc (Zn) and second other elements of interest: aluminium (Al), cobalt (Co), iron (Fe), manganese (Mn) and vanadium (V). However, the analysis of these elements was not mandatory.

Each NRL received samples prepared by the JRC and was supposed to carry out analysis according to its specific analytical protocol. It was assumed that the NRLs' measuring methods would have been typical of national implementations of heavy metal monitoring. In order to investigate the sources of possible analytical discrepancies, different sample types were proposed:

$S_1$ A liquid sample prepared using liquid Certified Reference Material (CRM) for heavy metals in 50-ml flasks made of perfluoroalkoxy copolymer (PFA). Each NRL was asked to carry out 6 replicate determinations to be repeated on 3 different days with 3 different calibrations (all together 18 different sub-samples). All results had to be reported after subtraction of the reagent blank.

13 Demonstration of equivalence of ambient air monitoring methods. Report by an EC Working group on Guidance for the Demonstration of Equivalence, http://ec.europa.eu/environment/air/pdf/equivalence_report3.pdf

$S_2$ A solution of a certified dust sample, digested by the JRC according to EN 14902[14]. The digested sample was diluted with MilliQ water in a 25-ml PFA flask. Each NRL was asked to carry out 6 replicate determinations. All results had to be reported after subtraction of the reagent blank.

$S_3$ A sample with a known mass (about 10 mg) of a dust CRM in a PFA vial that each participating laboratory had to digest and analyse. Each NRL was supposed to digest the whole sample and then to carry out six replicate determinations of heavy metals. The mass of heavy metals of $S_3$, expressed in ng, had to be blank-subtracted. It was requested to indicate the reagent blank and its standard deviation with units in ng/ml indicating the total volume of $S_3$.

$S_4$ A solution prepared by digestion of an exposed filter (generally Whatman quartz QMA 47 mm) sent in a 25 ml PFA flask. The digestion was carried out by JRC according to the procedure laid down in EN 14902. Each NRL was asked to carry out six replicate determinations of heavy metals in the solution. The results of $S_4$, expressed in ng/ml had to be blank-subtracted using the blank value determined for $S_5$ (see hereafter). The mass of heavy metals on the blank filter had to be divided by the volume of the flask (25 ml) before being subtracted.

$S_5$ One blank and one exposed filter (generally Whatman quartz QMA 47 mm in a Petri dish), had to be digested and analysed by the participating laboratory according to their standard operational procedure. Each NRL was asked to carry out six replicate determinations of heavy metals on the exposed filter repeated on three different days while six replicate determinations were asked for the blank only on one day. The mass of heavy metals of $S_5$, expressed in ng, had to be blank-subtracted.

# Preparation of samples

All glass flasks and PFA flasks/vials used for the preparation of samples and the digestion vessels of the microwave oven were cleaned according to EN 14902 (see Annex 1). Additionally, all PFA flasks (VIT-LAB GmbH - G) and vials were brand new. The reagents used in the preparation of the samples were all of ultrapure grade: nitric acid ($HNO_3$) 70% (J.T.Baker), hydrogen peroxide ($H_2O_2$) 30% (J.T.Baker) and hydrofluoric acid (HF) 49% (ROMIL – UpA) (see Annex 2). The reference values of $S_1$ and $S_2$ were close to the target value of the Daughter Directives.

**Sample $S_1$, a sub-sample of a diluted Certified Reference Material**

Two liquid CRMs (Romil 'PrimAg' ICP calibration mix BY14 and R14) were mixed together and diluted with MilliQ water to prepare the test sample $S_1$. It was prepared in the ERLAP's balance room where the temperature and relative humidity are continuously monitored and regulated at 20°C ± 1ºC and 50 ± 5%. Using two gravimetrically adjusted pipettes, 100 µl of BY14 and 900 µl of R14 were introduced in a PFA vial. The mixture of BY14 and R14 was transferred into a glass 2-liter flask, rinsing seven times the vial with MilliQ water. Subsequently, 10 ml of $HNO_3$ 70% were added. Finally, the flask was filled with MilliQ water. Aliquots of this solution were then transferred into 50-ml PFA flasks, all labelled '$S_1$'. Before sending the flasks, the caps of the 50-ml PFA flasks were cautiously screwed and then sealed with Para film. An example of the $S_1$ test sample is shown in Figure 2. The reference values of $S_1$ to be used for data treatment are given in Table 2. Details of the calculation of the reference values and their uncertainties

**Figure 2: $S_1$ sample**

**Figure 1: $S_2$ sample**

14 European standard, 2005. Ambient air quality—standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter. EN 14902, Brussels.

are given in Annex 3. Two methods, a volumetric and a gravimetric method, were used to determine the uncertainty of the reference values of $S_1$. For the data treatment presented hereafter, only the volumetric method of estimation of the uncertainty will be used.

### Sample $S_2$, a digested sample of a dust Certified Reference Material

$S_2$ was prepared using the NIST Standard Reference Material 1648. The NIST SRM 1648 was placed over night in an oven at 105 °C for drying and then kept in a desiccator. A portion of the NIST 1648 (about 150 mg) was weighed in the ERLAP's balance room directly in the digestion vessel which was closed just after weighing. The digestion (see Annex 4) was carried out using 8 ml nitric acid, 2 ml hydrogen peroxide and 0.5 ml hydrofluoric acid. After digestion the solution was completely transparent without any solid substrate. The solution in the Teflon vessel was transferred to a glass flask and completed to 1 litre with MilliQ water without any filtering. Aliquots were then transferred into 25 or 50 ml PFA flasks previously labelled with '$S_2$'. Before sending the flasks (see Figure 1), the caps of the flask were sealed with Para film. The reference values of $S_2$ to be used for the data treatment are given in Table 2. Details of the calculation of the reference values and their uncertainties are given in Annex 3.

**Table 2: Reference values of heavy metals in samples $S_1$ and $S_2$ with their expanded uncertainty. For $S_1$, two determinations are given, one using the volume of micropipette and one with the mass of CRMs (both gave equivalent reference values).**

| Samples, Elements | As | Cd | Ni | Pb | Zn | Cu | Cr | Mn | Co | V | Fe | Al |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$, ng.ml$^{-1}$, volume | 7.03±0.17 | 5.01±0.3 | 27.6±1.0 | 50.1±1.7 | 70.3±12.7 | 27.6±0.3 | 27.5* | 70.3* | 9.6* | 27.6* | | |
| $S_1$, ng.ml$^{-1}$, mass | 7.04±0.50 | 5.00 ±0.45 | 27.6±1.4 | 50.1±2.2 | 70.4±13.4 | 27.6±1.1 | 27.5* | 70.4* | 9.6* | 27.6* | | |
| S2, ng.ml$^{-1}$, | 17.5± 4.4 | 11.4±1.2 | 12.5±1.2 | 996±29 | 724±61 | 92.6±9.5 | 61.3* | 119* | | 19.3* | 5943* | 5198* |

**: the uncertainty is not reported as data on blank and digestion were missing*

### Sample $S_3$, a sample of dust Certified Reference Material

A sub-sample of a CRM was prepared for $S_3$ by introducing a small quantity of dust of the NIST SRM 1648 in a PFA vial. The NIST 1648 glass bottle was placed over night in an oven at 105 °C for drying and then stored in a desiccator. All PFA vials were cleaned according to the procedure given in Annex 1. Then the vials were dried with chemically filtered zero air and stored for several days in the weighing room at 20 ºC and 50 % of relative humidity before being weighed. During weighing it was also checked that the mass equilibrium was reached without water vapour exchange on the vials' walls. A label with a number was attached to every vial. A portion of the CRM was added in the vial which was immediately closed with its screwed lid and weighed again (the difference between these two weighings are given in Table 12). It was checked that the balance came back to its initial value when removing the vial from the pan of the balance, thus demonstrating that all the dust was in the vial and not on the pan of the balance. Before sending the samples, each vial was sealed with Para film.

**Figure 3: Vial for S3**

Each participant was requested to analyse the whole sample of dust. To ensure that the whole dust was removed from the vial for analysis, it was suggested:

1. to vigorously tap the container on a lab desk until no dust could be seen on the vial lid;
2. to open the vial just upon the digestion vessel used in the microwave oven and to introduce about a quarter of the acid solution needed for the digestion;
3. to close again the vial and to gently shaken it;
4. to transfer the acid solution of the vial into the digestion vessel;
5. to repeat these operations until the whole acid solution was used.

**Table 3: Digestion and analytical methods, traceability to standards, accreditation statute and estimation of measurement uncertainty.**

| Lab. | Digestion ($S_3$ and $S_5$) | Analytical method and calibration | Traceability | Accreditation | Uncertainty |
|---|---|---|---|---|---|
| 0 | No digestion | $S_5$ : As, Pb and Ni with 3D-ED-XRF, Cd with WD-XRF, Calibration curve | Filters prepared by aerosol generation with standard solutions (Merck AAS standard: 1000 ppm of As, Cd, Pb, Ni) | No | Repeatability only |
| 1 | EN 14902 with 8 ml $HNO_3$ and 2 m $H_2O_2$ | $S_{1-5}$: GFAAS, Calibration curve | Merck AAS standards solutions (1000 ppm of As, Cd, Pb, Ni) | No | Combined uncertainty based on precision and reproducibility |
| 2 | Microwave digestion with acids | HR-ICP-MS, Thermo Element2. | PE Pure Atomic Spectroscopy standards | No | Withdrawn, no results |
| 3 | EN 14902 with 8 ml sub boiled $HNO_3$ 65% and 2 ml $H_2O_2$ 30% pa, dilution to 50 ml in calibrated quartz flasks with MilliQ; then filtration through 150 mm folded filters in 50 ml PE flasks | ICP-MS (PE Elan DRC II) samples were measured against working curve, using matrix matched aqueous standards, Calibration curve | Plasma standard, Baker Instra Analyzed ICP standards, traceable to NIST SRM 3103a (As), 3108 (Cd), 3136 (Ni) and 3128 (Pb) | Yes | Calculation based on the Recovery of Reference material NIST 1648. |
| 4 | EN 14902 with 8 ml $HNO_3$ and 2 ml $H_2O_2$ | ICP-MS with simple mathematical corrections for interference, Calibration curve | PlasmaCal (SCPscience) Nist traceable, PlasmaCal 1000 ppm standard and QC standards are NIST traceable, garanteed accuracy to within plus or minus 1% | No | GUM method (k = 2) combining repeatability and bias from Quality Controls with a tolerance of ± 5% and assuming a rectangular distribution |
| 5 | Microwave digestion with 3 ml 65 % $HNO_3$; diluted to 25 ml with Re-$H_2O$ | GFAAS, Calibration curve for As and Ni, standard additions for Cd and Pb | MERCK AAS standard solutions (CertiPUR®) traceable to SRM from NIST | No | Full uncertainty not available |
| 6 | EN 14902 with 8 ml $HNO_3$ and 2 ml $H_2O_2$ | GFAAS, determination amount of metals using calibration curve | Standard solution IV (FLUKA) for calibration curve and ICP multielem. St. solution XVI and VIII (MERCK) for quality control | Yes for Cd and Cr | GUM method combining standard uncertainty of recovery, calibration and laboratory bias |
| 7 | S3: sample quantitatively transferred to a microwave vial for digestion, then evaporated to a droplet and mixed with 10 ml of 3% $HNO_3$. S5: Microwave digestion with 6 ml $HNO_3$ and 2 m $H_2O_2$, then concentration by evaporation | ICP-MS, Calibration curve | Std Analytika-Astasol; Merck Certipur and NIST 1648, | Yes, As, Cd, Cu, Mn, Ni, Pb in ambient air | Gum method with contribution of calibration (CRM certified uncertainty) and repeatability (n=12, 1 day) of CRM analysis. Four elements outside accreditation |
| 8 | High pressure digestion | As by GF-AAS and Cd, Ni, Pb, Zn, Cr, Mn, V, Fe, Cu by ICP-OES, Calibration curve | CPI international, traceability of the standards safeguarded by certified NIST SRM. | Yes for As, Pb, Cd, Ni, Cr, Fe, Zn in ambient air | Gum method with contribution of filter blank, sampling volume, digestion, dilution and spectroscopic analysis . |
| 9 | EN 14902 with 8 ml $HNO_3$ and 2 m $H_2O_2$ microwave digestion, max power 600W | ICP-MS, Rh as internal standard, Calibration curve | Perkin Elmer Multielement ICP-MS Calibration Std. 3, QA/QC ICP Multi XVI PE PurePlus | No | repeatability, reproducibility and bias taken into account |
| 10 | Microwave digestion | ICP-MS using Ge, Rh, Re as Internal Standards, Calibration curve | BDH QC-2 | No | No uncertainty reported |

| | | | | | |
|---|---|---|---|---|---|
| 11 | S3: 8 ml of $HNO_3$ (70 %) + 2ml $H_2O_2$ (30%) completed with MilliQ to 25 ml, S5: 0.5 ml HF (49%) evaporation on a hot plate at 70 – 80°C, then microwave digestion with 8 ml of $HNO_3$ (70 %) and 2ml $H_2O_2$ (30%) completed with MilliQ to 25 ml | S1, S2, S3: GFAAS for Cd, As and Ni, ICP-OES for Pb, S4 and S5: GFAAS, Calibration curve | Merck ICP multi-element Standard for calibration IV, Check: SPS-WW1 and WW2 Promochem and NIST 1648 | No | Uncertainty reported but without explanation on the estimation method |
| 12 | S3, S5, S6-8 Microwave According to EN 14902, S6-17 HF "cold" digestion method14F[15] | ICP-MS (PE Sciex Elan 6000), according to standard ASTM D 5673-96, Calibration curve | Calibration standards were gravimetrically prepared from Merck ICP Multi-element Standard Solution VI CertiPUR, which is traceable to NIST. The certified reference material NIES 8 was used in controlling the recovery rate of microwave digestion. | Yes for precipitation sample (Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn) | Expanded uncertainty calculated using systematic error and random error |
| 13 | No digestion | S1, $S_2$ and S4: ICP-MS, S3 and S5 PIXE | Sample 1, no full uncertainty. Sample 3 and5 , PIXE, full uncertainty, | PIXE accredited | Withdrawn, no results |
| 14 | Filters and dust samples were digested at temperatures up to 220°C using a CEM Mars X microwave, in 8 ml of 70% nitric acid and 2 ml 30% hydrogen peroxide. S3 was diluted to 500ml before analysis, with reagent blank. | ICP-MS (PerkinElmer Elan DRC II). Internal method fully compliant with EN 14902. Long tem drift correction using external standard and short term correction with internal standard (Ge, Rh, Re). For all sample solutions, 6 replicate analysis were performed. Arsenic was corrected for interference of ArCl and for matrix effects. Calibration curve | Calibration standards were prepared gravimetrically from NIST standard reference materials 3103a, 3108, 3136 and 3128. For calibration of all analysis, at least four gravimetrically-prepared calibration solutions were used | Yes for As, Cd, Cr, Cu, Fe, Pb, Mn, Ni, V, Zn | Analytical uncertainty calculated following the ISO-6143 approach where both calibration and response errors are used to estimate the calibration determined by weighted least squares regression technique. The uncertainty estimation comprises contributions from instrument repeatability, internal standard correction, uncertainty in the calibration standards and uncertainty in sample dilutions. |
| 15 | EN 14902 with 8 ml $HNO_3$ and 2 ml $H_2O_2$ | Anodic stripping voltammetry for Cd, Pb, Cu, Zn and As, adsorptive stripping voltammetry for Ni. Calibration by standard addition | Romil – PrimAg-xtra certified reference material and NIST 1648 | No | Expanded uncertainty calculated using the error contribution from the measurement and that from the calibration, repeatability, calibration standards, recovery (for S3,S5) |
| 16 | EN 14902 with 8 ml $HNO_3$ and 2 ml $H_2O_2$, Sub-boiled Ultrapure Nitric Acid 70% was used in all dilution steps after digestion. | ICP-MS (Agilent 7500) with correction of long tem drift correction using external standard and short term correction with internal standard (Sc-Y-Re). Using a collision cell for Fe and As. For all sample solutions, 3 replicates were performed. Calibration curve | Quality Control Standard CSTD solution (2 ng/g) was prepared and used every 11 steps of analysis to correct an eventual instrumental drift. NIST SRM 1648 was used as a second check. BDH Certified Calibration Standard 2 (10 µg/ml), ROMIL Certified Standards (Sc, Y, Re), | No | No uncertainty reported |

[15] Jalkanen, L.M. and Häsänen, E.K., Simple method for the dissolution of atmospheric aerosol samples for analysis by inductively coupled plasma mass spectrometry. *J. Anal. At. Spectrom.*, May 1996, Vol. 11 (365-369).

### Sample $S_4$, a solution prepared by digestion of an exposed filter

Seventeen low volume samplers (LVS) Derenda 3.1 operating according to EN 12341 were used in this IE. All the LVS had their flow adjusted at the JRC to have less than 2 % of deviation with a certified gas counter (Ritter – DKD certificate) before the field experiment. The relative humidity, pressure and temperature sensors were also checked in laboratory. Before each field test, the flow of all LVS was again checked using a flow meter (Rotameter).

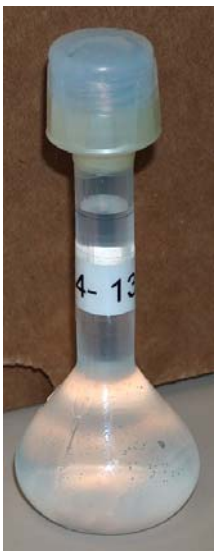

**Figure 4: Sample $S_4$**

The sampling site was a monitoring station in Milan (I), a urban background site operated by the "Agenzia Regionale per la Protezione dell'Ambiente della Lombardia" (ARPA) inside the Politecnico University of Milan (see Figure 6). The monitoring station is located in a park and near a football field. The traffic around the site was generally moderate with an increase in the late afternoon until the evening. Figure 6 shows the distribution of the LVSs at the sampling site.

All filters were conditioned for at least 48 hours in the balance room at 20 ºC and 50 % relative humidity as foreseen in EN 12341. The filters were weighed on 2 consecutive days to check that their mass was stable and the conditioning was continued in case of mass instability. Most of filters were Whatman QMA quartz 47 mm chosen for their low blank level of heavy metals. NRL nº13 and 14 asked for specific filters: 47mm PALL GN-4 Metricel Membrane filters (ester of cellulose). After field sampling of $PM_{10}$ all filters were conditioned again in the balance room before weighing (see results in Annex 7: Homogeneity of sampling PM10 with Low Volume Samplers). Finally, the filters were digested in a microwave oven according to Annex 4 with 8 ml of $HNO_3$ and 2 ml of $H_2O_2$. After digestion, the solution in the digestion vessel was transferred to a 25 ml PFA-volumetric flask and completed with MilliQ water. The flasks were labelled "$S_4$ plus the number of the digested filter" (see Figure 4). Before sending the flasks, the caps of the PFA flasks were sealed with Para film after being cautiously screwed. The assigned values of $S_4$ to be used in the data treatment are given in Table 4. Details of the calculation of the assigned values and their uncertainties are given in Annex 3.

**Table 4: Assigned values means and combined uncertainty for t $S_4$ and $S_5$**

| | *As* | *Cd* | *Ni* | *Pb* |
|---|---|---|---|---|
| S4, ng/ml | 5.1 ± 0.24 | 3.1 ± 0.15 | 35.9 ± 2.6 | 168.1 ± 3.6 |
| S5, ng | 120.2 ± 6.4 | 95.6 ± 6.2 | 469 ± 35 | 3841 ± 117 |

### Sample $S_5$, one blank and one exposed filter to be digested and analysed by the NRLs

For the preparation of sample $S_5$ the same procedure as for $S_4$ was applied. The filters were exposed at the same monitoring site on a different day and afterwards weighed in the ERLAP's balance room (see results in Annex 7: Homogeneity of sampling PM10 with Low Volume Samplers). A set of blanks was also prepared for this part of the test. After finishing the weighing, the Petri dishes containing the filters were sealed with Para film as shown in Figure 5. The assigned values of $S_5$ to be used in the data treatment are given in Table 4. Details of the calculation of the assigned values and their uncertainties are given in Annex 3.

**Figure 5: Example of a $S_5$ sample**

**Figure 6: Monitoring station in Milan (I)**

# Data treatment

The analytical results of all participants are given in Table 17 to Table 24 for As, Cd, Ni and Pb and in Table 25 to Table 36 for the other elements. The data evaluation was carried out according to ISO Guide 43-1[16], ISO 13528[17] and ISO 5725[18]. Several data evaluation methods were used according to the objectives of the IE:

1. The z' score method was used to demonstrate the capacity of NRLs to comply with the DQO of the 1st and 4th Daughter Directive; the z' score was calculated for all NRLs participating in the IE.
2. The normalized deviation (En) method was used to check whether the difference between the NRL values and the assigned/reference values remains within uncertainties. The En values were only calculated for laboratories reporting their uncertainty of measurements to demonstrate that.
3. The repeatability (r) and reproducibility (R) of the method of analysis were determined according to ISO 5725-2[18]. These statistics were used to give an overall assessment of the state of the art of heavy metals monitoring in EU. For each laboratory the within-day repeatability and between-day reproducibility were evaluated.
4. Evaluation of the contribution of digestion, analytical method and calibration to the overall uncertainty of heavy metal determination.

[16] *International Organisation for Standardisation, 1997. Proficiency testing by interlaboratory comparisons—Part 1. development and operation of proficiency testing schemes. ISO Guide 43_1, Geneva.*

[17] *ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons, Geneva, CH*

[18] *ISO 5725-2:1994Accuracy (trueness and precision) of measurement methods and results -- Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method, Geneva, CH*

**z' score**

The z' scores were calculated according to ISO 13528 using Eq. 1 where x is a NRLs' value, X is the reference/assigned value, $\sigma_p$ is the "fitness-for-purpose-based standard deviation for proficiency assessment" and $u_X$ is the standard uncertainty of the reference/assigned value. The z'-score evaluation allows the following criteria to be used for the assessment of the results:

- $-2 \leq z' \leq 2$ are designated satisfactory.
- $-3 \leq z' < -2$ or $2 < z' \leq 3$ are designated questionable.
- $z < -3$ or $z > 3$ are designated unsatisfactory. Scores falling in this range indicate that the cause of the event should be investigated and remedied.

$$z' = \frac{x - X}{\sqrt{\sigma_p^2 + u_X^2}} \qquad \text{Eq. 1}$$

The reference/assigned values X and its expanded uncertainty $U_X$ are given in Table 2 for samples $S_1$ and $S_2$, in Annex 6 for $S_3$ and in Table 4 for $S_4$ and $S_5$. The fitness-for-purpose-based standard deviation, $\sigma_p$, was estimated according to Eq. 2 using the DQOs of the 1st and 4th Daughter Directives (25 % for Pb and 40 % for Cd, As and Ni) and the contribution of the standard uncertainties of sampling ($u_s$), digestion ($u_e$) and interference/matrix effects ($u_m$). In Eq. 2, $\sigma_{p,r}$ is the relative fitness-for-purpose-based standard deviation and is defined by $\sigma_{p,r} = \sigma_p/X$ and $u_{s,r}$, $u_{e,r}$ and $u_{m,r}$ are the relative standard uncertainty of sampling, digestion and interference/matrix effects. They are defined by $u_{s,r} = u_s/X$, $u_{e,r} = u_e/X$ and $u_{m,r} = u_m/X$.

$$S_5 \text{ and } S_3 : \sigma_{p,r} = \left( DQO^2 \Big/ 4 - u_{s,r}^2 \right)^{\frac{1}{2}}$$

$$S_4 \text{ and } S_2 : \sigma_{p,r} = \left( DQO^2 \Big/ 4 - u_{s,r}^2 - u_{e,r}^2 \right)^{\frac{1}{2}} \qquad \text{Eq. 2}$$

$$S_1 : \sigma_{p,r} = \left( DQO^2 \Big/ 4 - u_{s,r}^2 - u_{e,r}^2 - u_{m,r}^2 \right)^{\frac{1}{2}}$$

**Table 5: Relative fitness-for-purpose-based standard deviation $\sigma_{p,r}$ used in the calculation of z' scores for $S_1$ to $S_5$ calculated using the relative standard uncertainty of sampling ($u_{s,r}$), digestion ($u_{e,r}$) and interference/matrix effect ($u_{m,r}$)**

| | DQO | $u_{s,r}$ | $\sigma_{p,r}$ for $S_5$,$S_3$ | $u_{e,r}$ | $\sigma_{p,r}$ for $S_4$,$S_2$ | $u_{m,r}$ | $\sigma_{p,r}$ for $S_1$ |
|---|---|---|---|---|---|---|---|
| As | 40% | 4.7% | 19.4% | 12.9% | 14.6% | 12.9% | 6.7% |
| Cd | 40% | 4.7% | 19.4% | 9.9% | 16.7% | 2.9% | 16.5% |
| Ni | 40% | 4.7% | 19.4% | 12.3% | 15.1% | 6.9% | 13.4% |
| Pb | 25% | 4.7% | 11.6% | 6.7% | 9.5% | 3.8% | 8.6% |

The test samples $S_5$ and $S_3$ had to be analysed and digested by each NRL. Therefore, $\sigma_{p,r}$ was estimated using Eq. 2 but only subtracting $u_{s,r}$ from the DQO thus without contribution from digestion and interference/matrix effects. $u_{s,r}$ (4.7 %) was estimated by the quadratic sum of the repeatability of $PM_{10}$ of the 17 LVS (RSD 4 %, see Annex 7: Homogeneity of sampling $PM_{10}$ with Low Volume Samplers), the interval of tolerance of the flow calibration of the LVS (2 % variation) and the uncertainty of the balance used to weigh the loaded and blank filters (1%). The basis for relying on the mass scattering to estimate the heavy metal sampling errors is that heavy metals on filters are not expected to undergo volatilisation during sampling or storage.

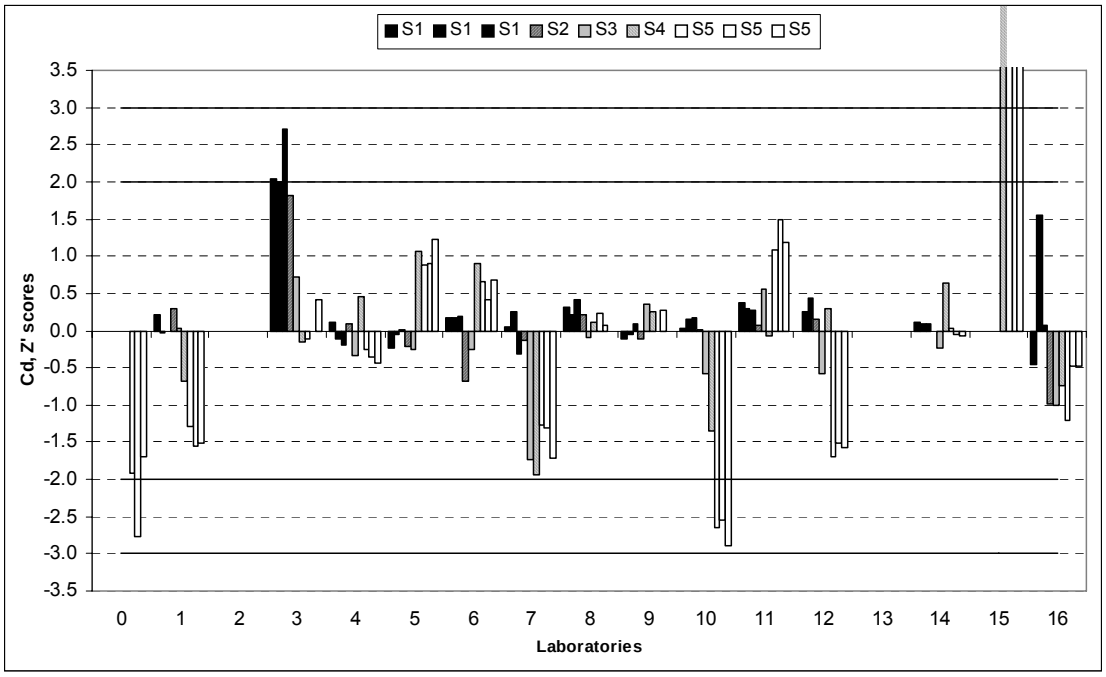


**Figure 7: z' score for Cd**

*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

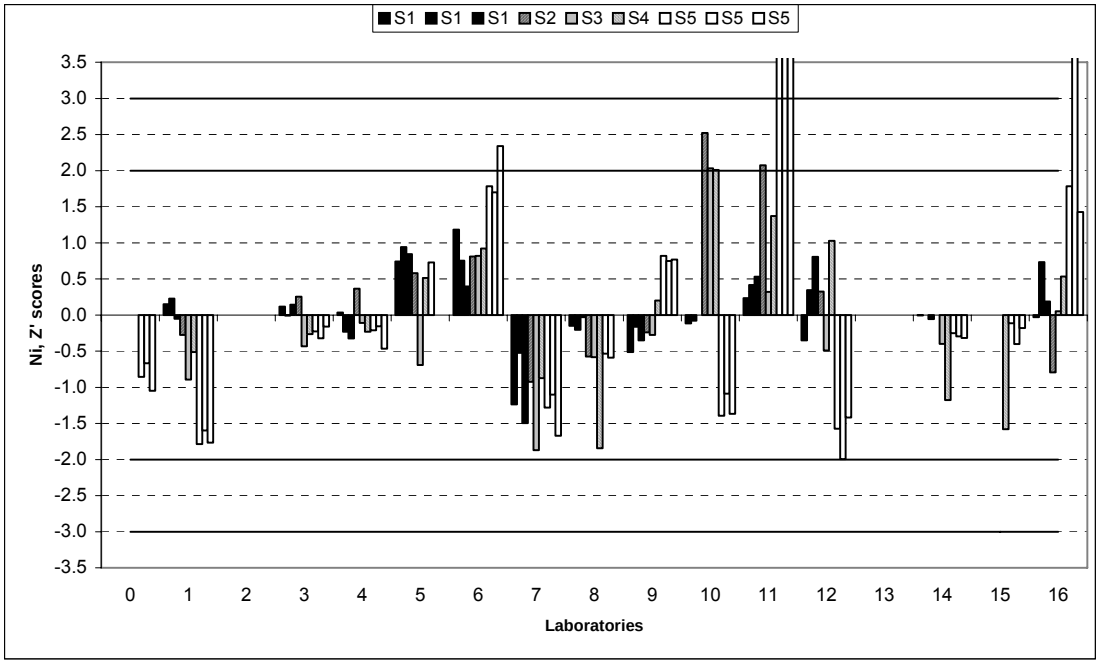


**Figure 8: z' score for Ni**

*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

For test samples $S_4$ and $S_2$, $\sigma_{p,r}$ was estimated by subtracting the relative standard uncertainty of digestion $u_{e,r}$ from $\sigma_{p,r}$ of $S_5$ and $S_3$. $u_{e,r}$ was estimated by the average of the ratios of NRLs values and reference value for $S_3$ out of the same ratio for $S_2$ (see Table 10). Finally, for $S_1$, $\sigma_{p,r}$ was estimated by subtracting the relative standard uncertainty due to matrix effects ($u_{m,r}$), from $\sigma_{p,r}$ of $S_4$ and $S_2$. $u_{m,r}$ was estimated by the average of the ratios of NRLs values and reference value for $S_2$ out of the same ratio for $S_1$ (see Table 10). All $\sigma_{p,r}$ values are given in Table 5 for all test samples. The results of z'-score evaluation for As, Cd, Ni and Pb are shown in Figure 7 to Figure 9. They are presented in bar plots in which z'-scores of each participant are grouped together.

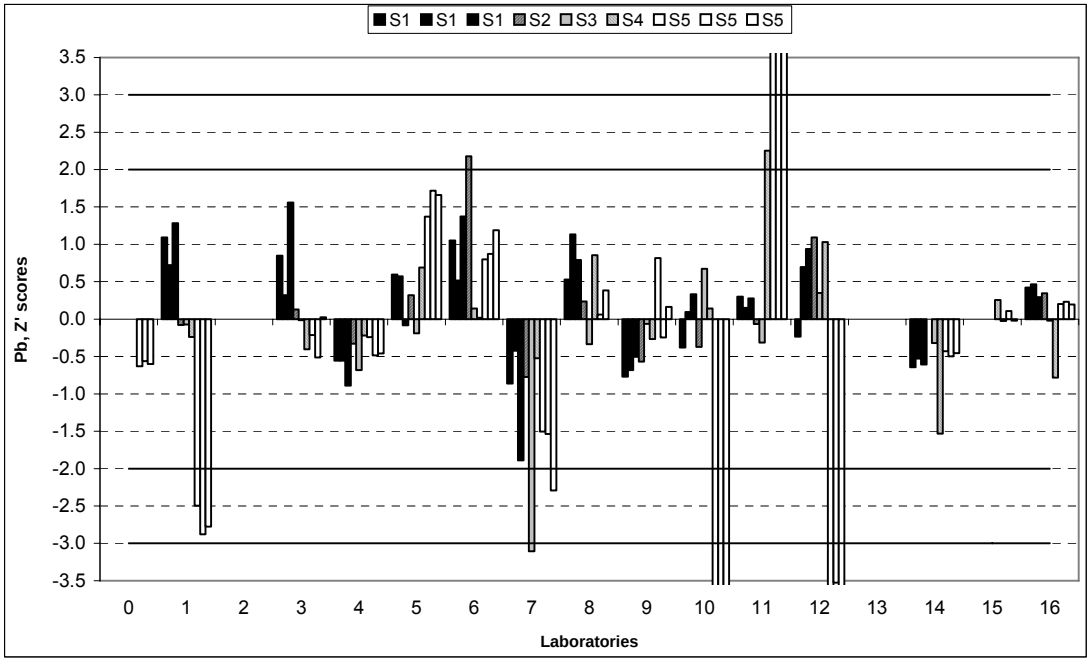


**Figure 9: z' score for Pb**

*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

In order to find possible explanations for high z' score values, Table 37 presents for each NRL their values of reagent blank value and blank filter with standard deviations. z'scores were also calculated for Zn, Cu , Cr, Mn and V following the same approach as for As, Cd, Ni and Pb. However, these elements are not regulated by the European Directives. In the absence of guidance in the European legislation, the EMEP Data Quality Objective of 25 % given in the EMEP manual[19] was used. In Figure 22 to Figure 26, the z'score for Zn, Cu, Cr, Mn and V are given. It was not possible to calculate any z' score first for Co because of the lack of certified value for samples $S_2$ and $S_3$ and second for Fe since very little data were reported by participants. Since the digestion was found incomplete for Cr, the data treatment had to be modified using the following values for $\sigma_{p,r}$, the relative fitness-for-purpose standard deviations: 12 % for $S_5$ and $S_3$, 10 % for $S_4$ and $S_2$ and 7.5 % for $S_1$.

## En method

The Normalized Deviations (En) are calculated according to ISO guide 43-1 using Eq. 3 where x are NRLs results with claimed expanded uncertainty $U_x$ while X is the reference/assigned value with expanded uncertainty $U_X$. The reference/assigned values X and uncertainties are given in Table 2 for samples $S_1$ and $S_2$, in Annex 6 for $S_3$ and in Table 4 for $S_4$ and $S_5$.

$$E_n = \frac{x - X}{\sqrt{U_x^2 + U_X^2}} \quad \text{Eq. 3}$$

[19] EMEP Manual for sampling and chemical analysis, EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe, http://www.nilu.no/projects/ccc/manual/index.html

Laboratories 1, 3, 4, 6, 7, 8, 9, 11, 12, 14 and 15 reported their relative expanded uncertainty of measurements $U_{x,r} = U_x/x$ given in Table 6. |En| numbers smaller than 1 indicate that the difference between NRLs value and reference or assigned values are within uncertainties (see Figure 10). Figure 11 to Figure 14 allow observing the extent of differences (x –X) and compare then with the quadratic sum of analytical and claimed uncertainties ($\sqrt{U_x^2 + U_X^2}$). For $S_1$ and $S_5$, the average of the replicate tests and uncertainties carried out on three different days were used. For NRL15 the En numbers are not plotted for $S_1$, $S_2$ and $S_3$ because the laboratory was aware of the reference values before analysis while the En values for $S_4$ and $S_5$ are plotted to show if the voltammetric values are consistent with the estimated uncertainty.

**Table 6: Relative expanded uncertainties ($U_{x,r}$) claimed by the NRLs for As , Cd, Ni and Pb**

| As | S1 | S2 | S3 | S4 | S5 |
|---|---|---|---|---|---|
| NRL 1 | 4.9% | 4.9% | 4.9% | 4.9% | 4.9% |
| NRL 3 | 10.3% | 10.3% | 10.3% | 10.3% | 10.3% |
| NRL 4 | 10.3% | 8.1% | 15.7% | 7.7% | 14.4% |
| NRL 6 | | 18.3% | 14.1% | 52.0% | 15.5% |
| NRL 7 | 20.0% | 20.0% | 20.0% | 20.0% | 20.0% |
| NRL 8 | 18.1% | 18.1% | 18.1% | 18.1% | 18.1% |
| NRL 9 | 16.0% | 16.1% | 16.6% | 16.0% | 16.0% |
| NRL 11 | 20.4% | 20.4% | 20.4% | 20.4% | 20.4% |
| NRL 12 | 20.0% | 20.0% | 30.0% | 20.0% | 30.0% |
| NRL 14 | 15.9% | | 10.2% | 26.2% | 31.2% |
| NRL 15 | 11.0% | 6.1% | 6.4% | 17.5% | |

| As | S1 | S2 | S3 | S4 | S5 |
|---|---|---|---|---|---|
| NRL 1 | 4.9% | 4.9% | 4.9% | 4.9% | 4.9% |
| NRL 3 | 10.3% | 10.3% | 10.3% | 10.3% | 10.3% |
| NRL 4 | 10.3% | 8.1% | 15.7% | 7.7% | 14.4% |
| NRL 6 | | 18.3% | 14.1% | 52.0% | 15.5% |
| NRL 7 | 20.0% | 20.0% | 20.0% | 20.0% | 20.0% |
| NRL 8 | 18.1% | 18.1% | 18.1% | 18.1% | 18.1% |
| NRL 9 | 16.0% | 16.1% | 16.6% | 16.0% | 16.0% |
| NRL 11 | 20.4% | 20.4% | 20.4% | 20.4% | 20.4% |
| NRL 12 | 20.0% | 20.0% | 30.0% | 20.0% | 30.0% |
| NRL 14 | 15.9% | | 10.2% | 26.2% | 31.2% |
| NRL 15 | 11.0% | 6.1% | 6.4% | 17.5% | |

| As | S1 | S2 | S3 | S4 | S5 |
|---|---|---|---|---|---|
| NRL 1 | 4.9% | 4.9% | 4.9% | 4.9% | 4.9% |
| NRL 3 | 10.3% | 10.3% | 10.3% | 10.3% | 10.3% |
| NRL 4 | 10.3% | 8.1% | 15.7% | 7.7% | 14.4% |
| NRL 6 | | 18.3% | 14.1% | 52.0% | 15.5% |
| NRL 7 | 20.0% | 20.0% | 20.0% | 20.0% | 20.0% |
| NRL 8 | 18.1% | 18.1% | 18.1% | 18.1% | 18.1% |
| NRL 9 | 16.0% | 16.1% | 16.6% | 16.0% | 16.0% |
| NRL 11 | 20.4% | 20.4% | 20.4% | 20.4% | 20.4% |
| NRL 12 | 20.0% | 20.0% | 30.0% | 20.0% | 30.0% |
| NRL 14 | 15.9% | | 10.2% | 26.2% | 31.2% |
| NRL 15 | 11.0% | 6.1% | 6.4% | 17.5% | |

*NRL 1 and 8 reported their uncertainty once the results were distributed. The uncertainty of NRL 15 for S1, S2 and S3 are given for information only as the laboratory knew the reference values and no En treatment is carried out*

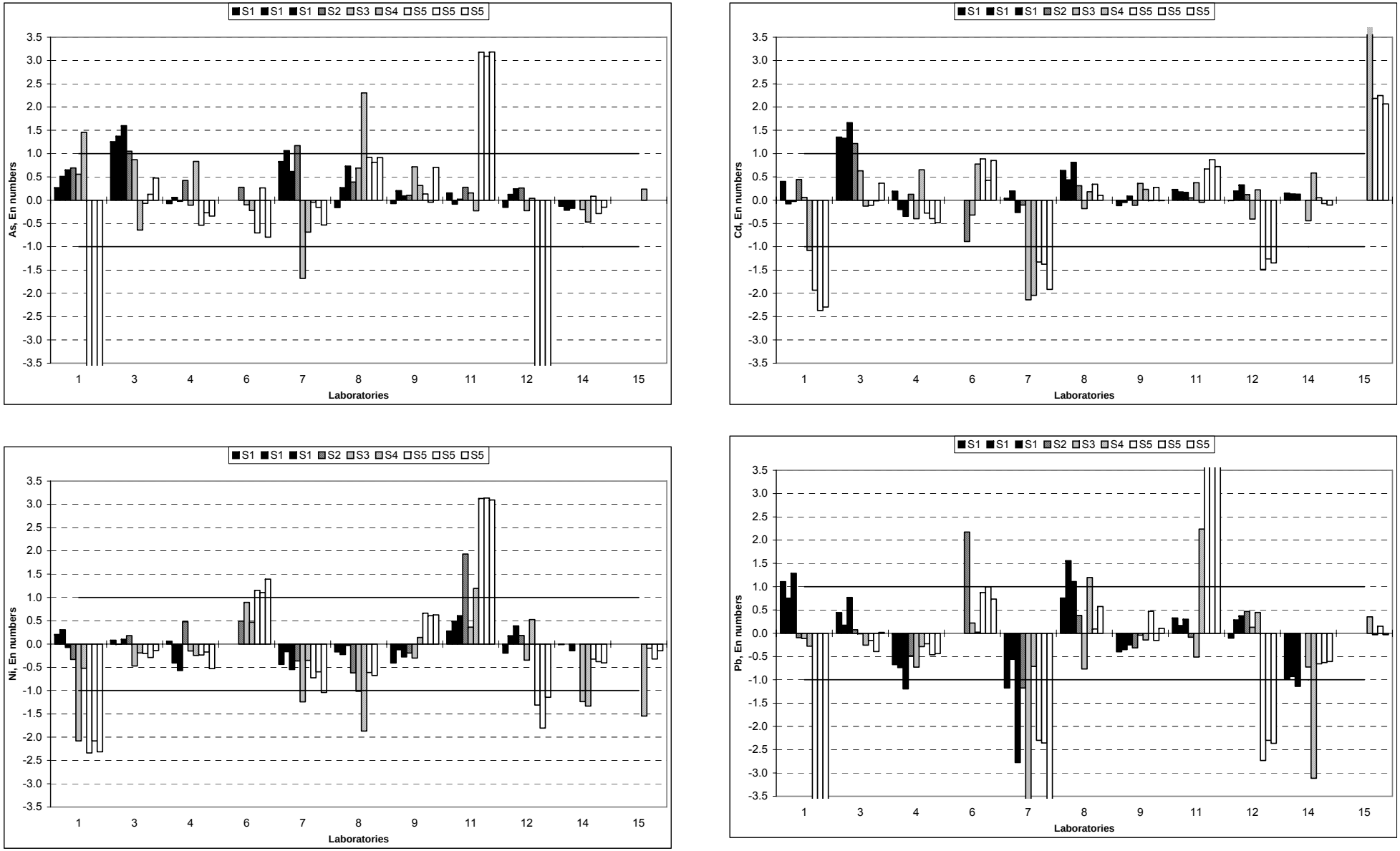


**Figure 10: En numbers for As , Cd, Ni and Pb**

*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

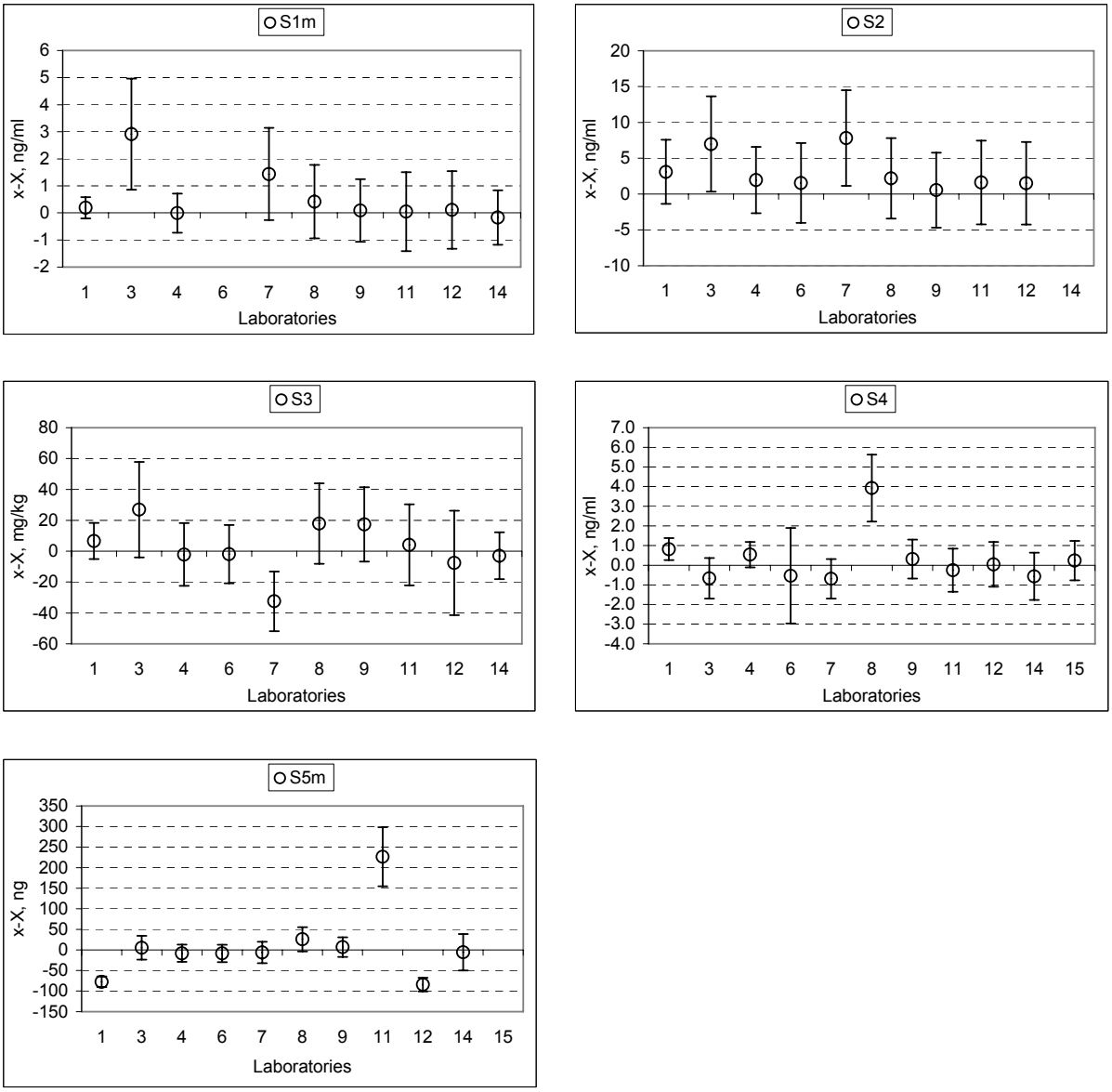


**Figure 11: Extent of differences between NRL results and reference values (x –X) for As. The error bars show the square root of the quadratic sum of the expanded uncertainty of reference values plus the NRLs' claimed expanded uncertainty ($\sqrt{U_x^2 + U_X^2}$ ).**

*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

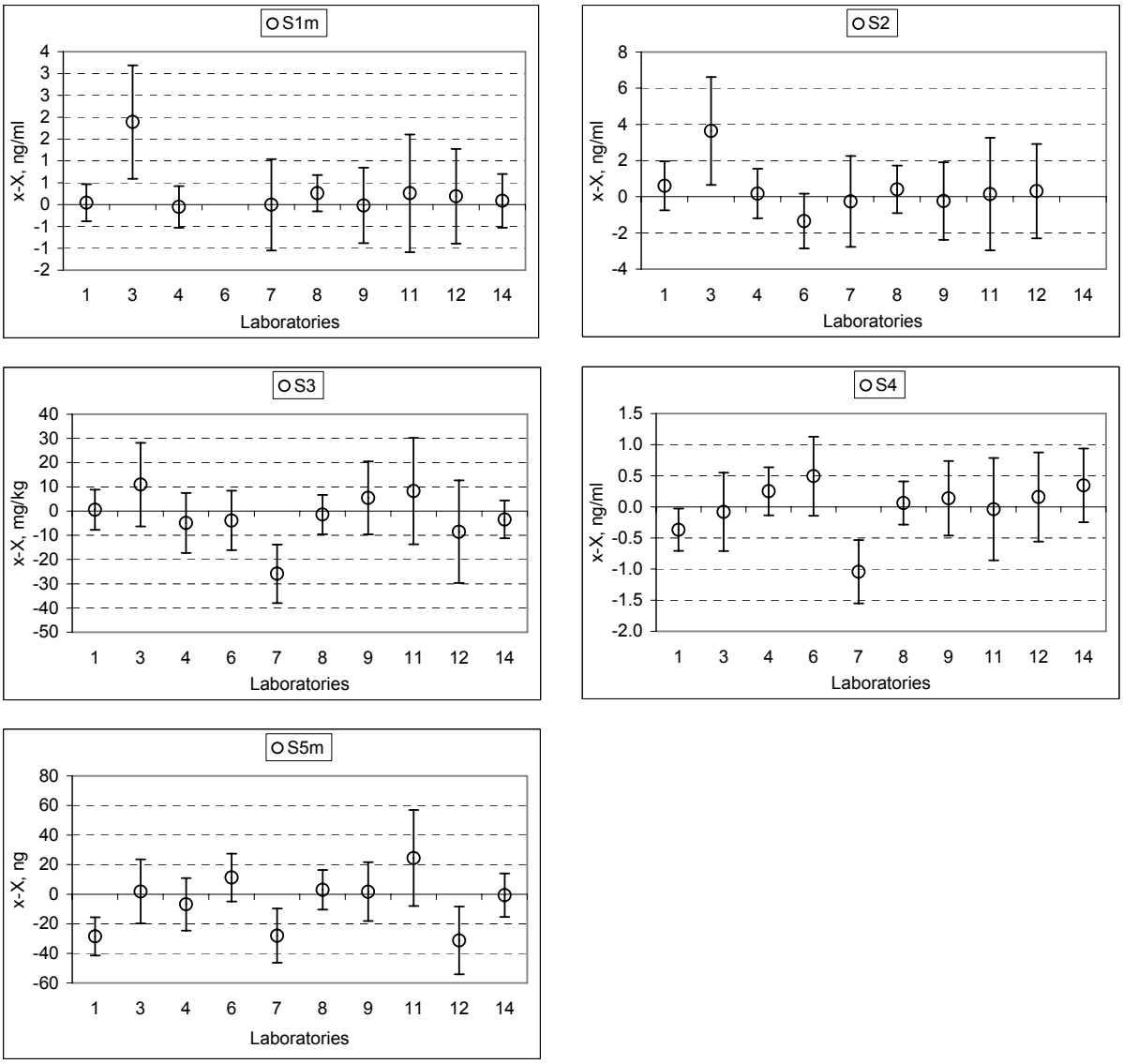


**Figure 12: Extent of differences between NRL results and reference values (x –X) for Cd. The error bars show the square root of the quadratic sum of the expanded uncertainty of reference values plus the NRLs' claimed expanded uncertainty ($\sqrt{U_x^2 + U_X^2}$ ).**

*In $S_4$ and $S_5$, NRL 15 is discarded in order to keep value in range ($S_4$ : x-X = 24 ng/ml and $S_5$ : x -X = 240 ng) For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

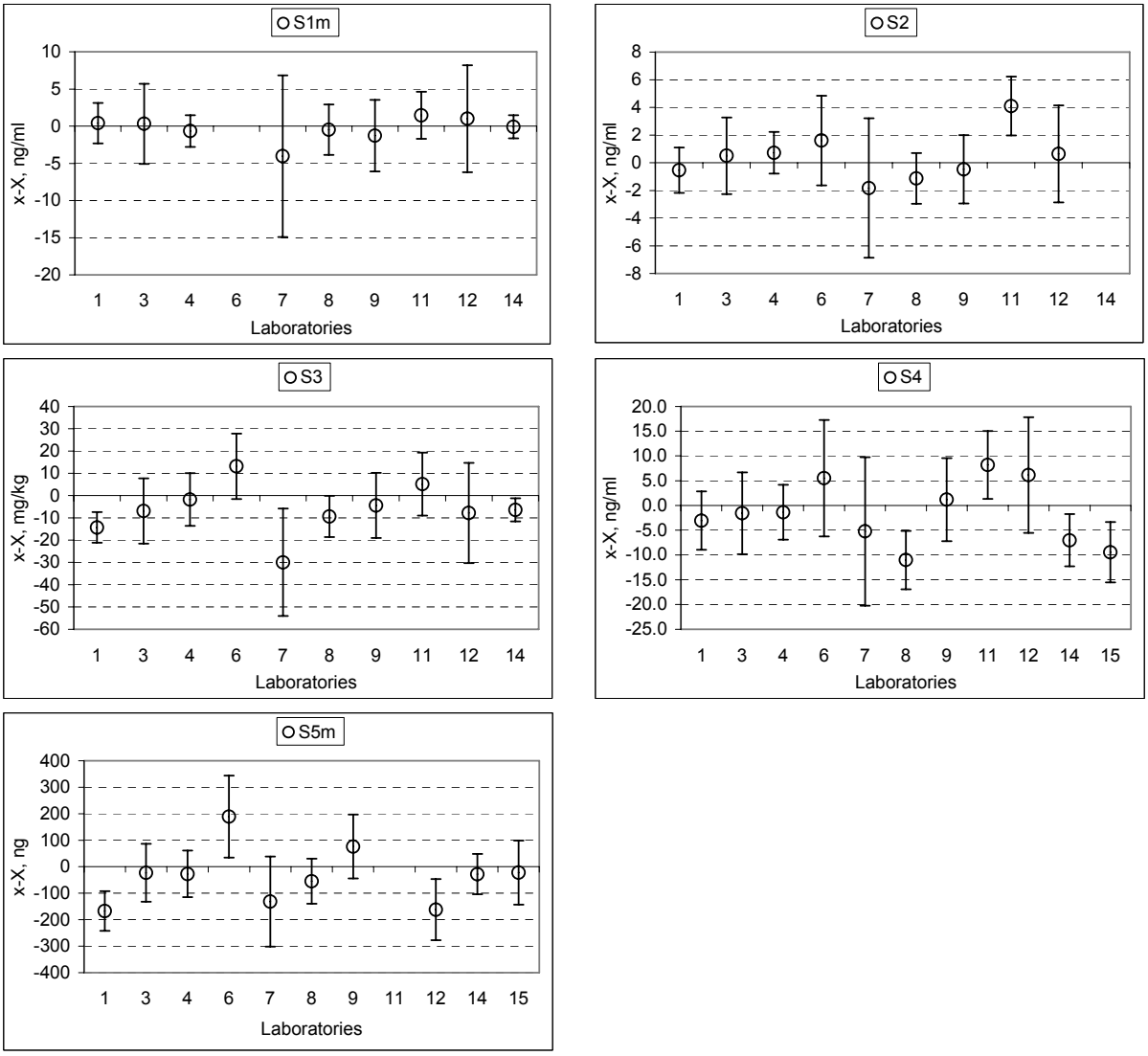


**Figure 13: Extent of differences between NRL results and reference values (x –X) for Ni. The error bars show the square root of the quadratic sum of the expanded uncertainty of reference values plus the NRLs' claimed expanded uncertainty ($\sqrt{U_x^2 + U_X^2}$ ).**

*In S5, NRL 11 is discarded in order to keep value in range (x-X = 8800 ng)*
*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

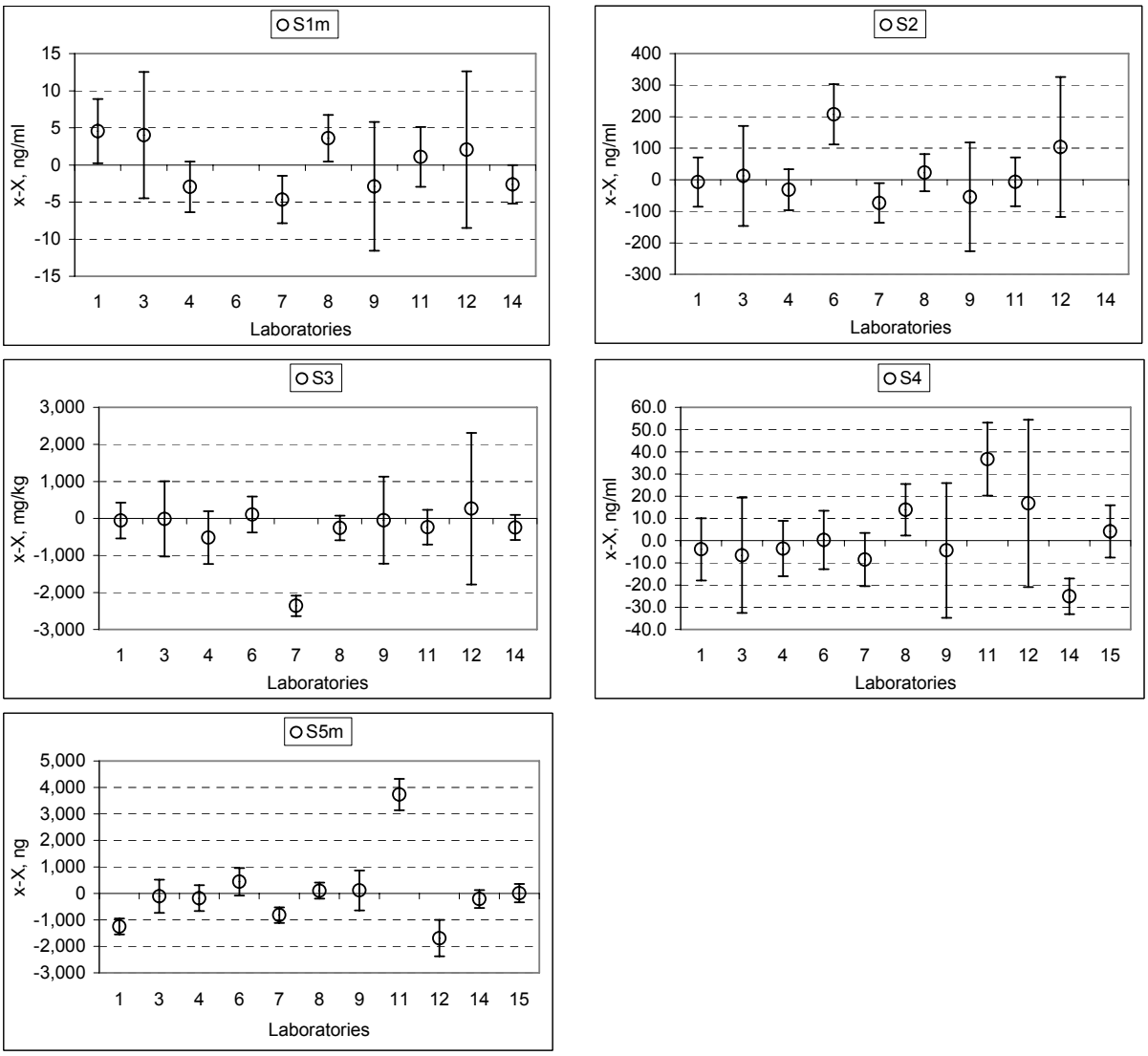


**Figure 14: Extent of differences between NRL results and reference values (x –X) for Pb. The error bars show the square root of the quadratic sum of the expanded uncertainty of reference values plus the NRLs' claimed expanded uncertainty ($\sqrt{U_x^2 + U_X^2}$ ).**

*For $S_4$ and $S_5$, NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

## Repeatability – reproducibility

ISO 5725 was applied for the determination of repeatability and reproducibility of the methods of measurements for each test sample (see Table 7). Two determinations were performed: in the 1st one the outliers were included in the calculation while in the 2nd one the outliers were discarded (see details Annex 9: Scrutiny of results for consistency and statistical outliers).

*Repeatability – reproducibility with different methods of measurements*

**Table 7: Repeatability (r) and reproducibility (R) due to measurement methods variability, for each test sample for As, Cd, Ni and Pb**

| | | | Outliers included | | Outliers discarded | |
|---|---|---|---|---|---|---|
| | Samples | m | r | R | r | R |
| As | $S_1$, ng $ml^{-1}$ | 7.4 | 14.4% | 36.1% | 9% | 38% |
| | $S_1$, ng $ml^{-1}$ | 7.6 | 15.0% | 35.9% | 10% | 37% |
| | $S_1$, ng $ml^{-1}$ | 7.6 | 11.5% | 40.2% | 8% | 41% |
| | $S_2$, ng $ml^{-1}$ | 20.2 | 9.6% | 39.7% | 8% | 42% |
| | $S_3$, mg $kg^{-1}$ | 116.2 | 11.8% | 38.3% | 8% | 45% |
| | $S_4$, ng $ml^{-1}$ | 5.4 | 15.5% | 67.2% | 12% | 41% |
| | $S_5$, ng | 120 | 33% | 189% | 19% | 50% |
| | $S_5$, ng | 118 | 24% | 176% | 17% | 43% |
| | $S_5$, ng | 122 | 35% | 183% | 21% | 45% |
| Cd | $S_1$, ng $ml^{-1}$ | 5.2 | 8% | 28% | 7% | 13% |
| | $S_1$, ng $ml^{-1}$ | 5.3 | 6% | 29% | 6% | 8% |
| | $S_1$, ng $ml^{-1}$ | 5.3 | 7% | 33% | 5% | 11% |
| | $S_2$, ng $ml^{-1}$ | 11.4 | 5% | 33% | 4% | 21% |
| | $S_3$, mg $kg^{-1}$ | 70.3 | 9% | 40% | 5% | 41% |
| | $S_4$, ng $ml^{-1}$ | 4.8 | 16% | 380% | 7% | 46% |
| | $S_5$, ng | 100.7 | 15% | 181% | 9% | 51% |
| | $S_5$, ng | 100.9 | 14% | 183% | 7% | 52% |
| | $S_5$, ng | 100.9 | 15% | 178% | 12% | 60% |
| Ni | $S_1$, ng $ml^{-1}$ | 27.6 | 7% | 22% | 5% | 23% |
| | $S_1$, ng $ml^{-1}$ | 28.2 | 7% | 17% | 6% | 16% |
| | $S_1$, ng $ml^{-1}$ | 27.8 | 7% | 23% | 5% | 23% |
| | $S_2$, ng $ml^{-1}$ | 12.9 | 7% | 47% | 6% | 48% |
| | $S_3$, mg $kg^{-1}$ | 78.8 | 9% | 52% | 5% | 56% |
| | $S_4$, ng $ml^{-1}$ | 35.9 | 9% | 54% | 8% | 55% |
| | $S_5$, ng | 1052.3 | 39% | 631% | 7% | 66% |
| | $S_5$, ng | 1141.4 | 90% | 645% | 8% | 58% |
| | $S_5$, ng | 1015.8 | 68% | 585% | 5% | 79% |
| Pb | $S_1$, ng $ml^{-1}$ | 50.4 | 6% | 18% | 6% | 18% |
| | $S_1$, ng $ml^{-1}$ | 50.9 | 5% | 14% | 5% | 15% |
| | $S_1$, ng $ml^{-1}$ | 51.0 | 6% | 24% | 6% | 25% |
| | $S_2$, ng $ml^{-1}$ | 1011.4 | 4% | 21% | 3% | 21% |
| | $S_3$, mg $kg^{-1}$ | 6344.1 | 5% | 30% | 4% | 12% |
| | $S_4$, ng $ml^{-1}$ | 169.6 | 5% | 25% | 5% | 25% |
| | $S_5$, ng | 3782.4 | 8% | 96% | 5% | 36% |
| | $S_5$, ng | 3763.5 | 6% | 97% | 5% | 41% |
| | $S_5$, ng | 3754.0 | 7% | 100% | 8% | 46% |

*Repeatability – reproducibility of measurements carried out on different days and calibrations*

**Table 8: Repeatability (r) and reproducibility (R) due to between-days variability, for each test sample for As, Cd, Ni and Pb per laboratories**

| | As | | | | Cd | | | | Ni | | | | Pb | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S1 | | S5 | | S1 | | S5 | | S1 | | S5 | | S1 | | S5 | |
| | r% | R% | r% | R% | r% | R% | r% | R% | r% | R% | r% | R% | r% | R% | r% | R% |
| NRL 0 | | | 27% | 49% | | | 18% | 61% | | | 3.3% | 14% | | | 0.9% | 2% |
| NRL 1 | 11% | 11% | 18% | 32% | 4% | 8% | 5% | 13% | 3.8% | 6% | 2.3% | 10% | 4.4% | 8% | 0.7% | 10% |
| NRL 2 | | | | | | | | | | | | | | | | |
| NRL 3 | 4% | 15% | 6% | 19% | 4% | 14% | 6% | 17% | 3.9% | 5% | 1.6% | 5% | 4.1% | 15% | 0.6% | 9% |
| NRL 4 | 28% | 28% | 8% | 10% | 16% | 17% | 6% | 8% | 13.4% | 14% | 2.2% | 11% | 8.3% | 9% | 0.6% | 5% |
| NRL 5 | 10% | 11% | 6% | 13% | 3% | 7% | 4% | 10% | 12.0% | 12% | 1.9% | 2% | 6.3% | 11% | 0.6% | 5% |
| NRL 6 | 4% | 9% | 4% | 31% | 4% | 4% | 4% | 8% | 7.0% | 15% | 1.3% | 15% | 4.0% | 11% | 0.6% | 6% |
| NRL 7 | 6% | 16% | 5% | 16% | 8% | 15% | 5% | 21% | 5.4% | 23% | 1.8% | 24% | 7.1% | 22% | 0.5% | 19% |
| NRL 8 | 14% | 28% | 7% | 8% | 8% | 9% | 5% | 8% | 4.8% | 6% | 2.1% | 3% | 7.3% | 10% | 0.5% | 8% |
| NRL 9 | 6% | 8% | 5% | 23% | 7% | 8% | 6% | 11% | 5.6% | 9% | 2.5% | 3% | 4.3% | 5% | 0.9% | 18% |
| NRL 10 | 14% | 23% | 7% | 10% | 4% | 5% | 16% | 27% | 2.5% | 3% | 1.9% | 14% | 1.9% | 9% | 0.6% | 5% |
| NRL 11 | 26% | 26% | 5% | 9% | 7% | 7% | 3% | 10% | 8.4% | 9% | 0.9% | 34% | 4.9% | 5% | 0.4% | 2% |
| NRL 12 | 9% | 14% | 10% | 51% | 7% | 12% | 6% | 10% | 7.2% | 22% | 3.9% | 27% | 7.2% | 16% | 0.9% | 12% |
| NRL 13 | | | | | | | | | | | | | | | | |
| NRL 14 | 6% | 6% | 5% | 22% | 3% | 3% | 3% | 5% | 2.9% | 3% | 1.5% | 3% | 5.5% | 5% | 0.5% | 1% |
| NRL 15 | 19% | 31% | | | 8% | 12% | 3% | 8% | 9.3% | 10% | 2.2% | 10% | 6.6% | 8% | 0.7% | 3% |
| NRL 16 | 10% | 38% | 6% | 25% | 7% | 47% | 5% | 29% | 2.2% | 15% | 1.1% | 46% | 2.4% | 3% | 0.4% | 1% |

## Influence of the choice of the analytical methods on the bias of analytical results

In order to see the influence of the analytical methods on the results, the relative bias with standard deviation was plotted against the different methods involved in the IE. The results are presented in Figure 15 to Figure 18. It is not possible to show a significant bias for a specific method of analysis out of these graphs. This shows that the quality of the results could be influenced by the implementation of different methods by each participant.

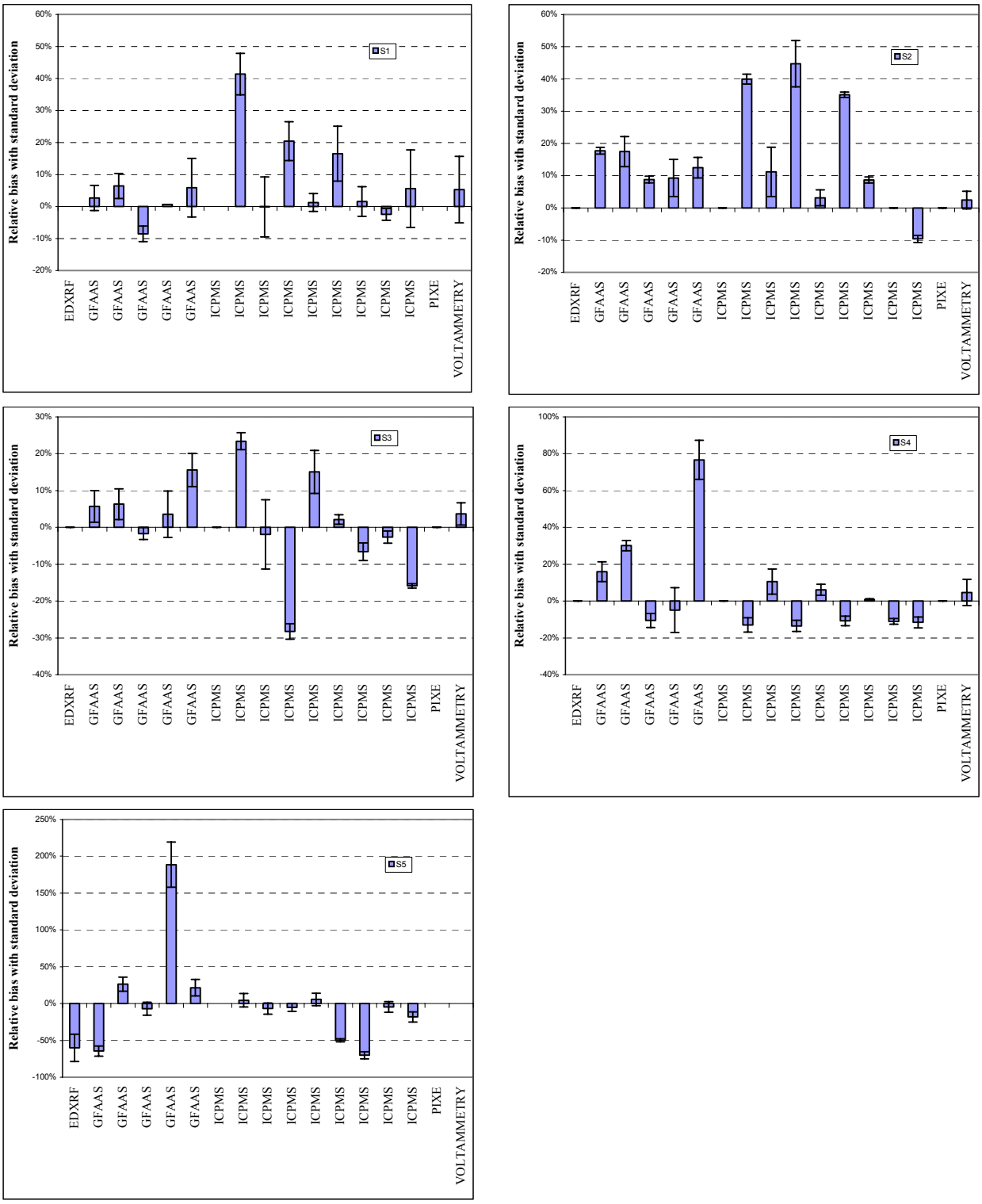


**Figure 15: Relative bias between reference values of test samples and NRL values grouped by measuring methods for As**

*The reference values were known to the laboratory using Voltammetry S1, S2 and S3.*

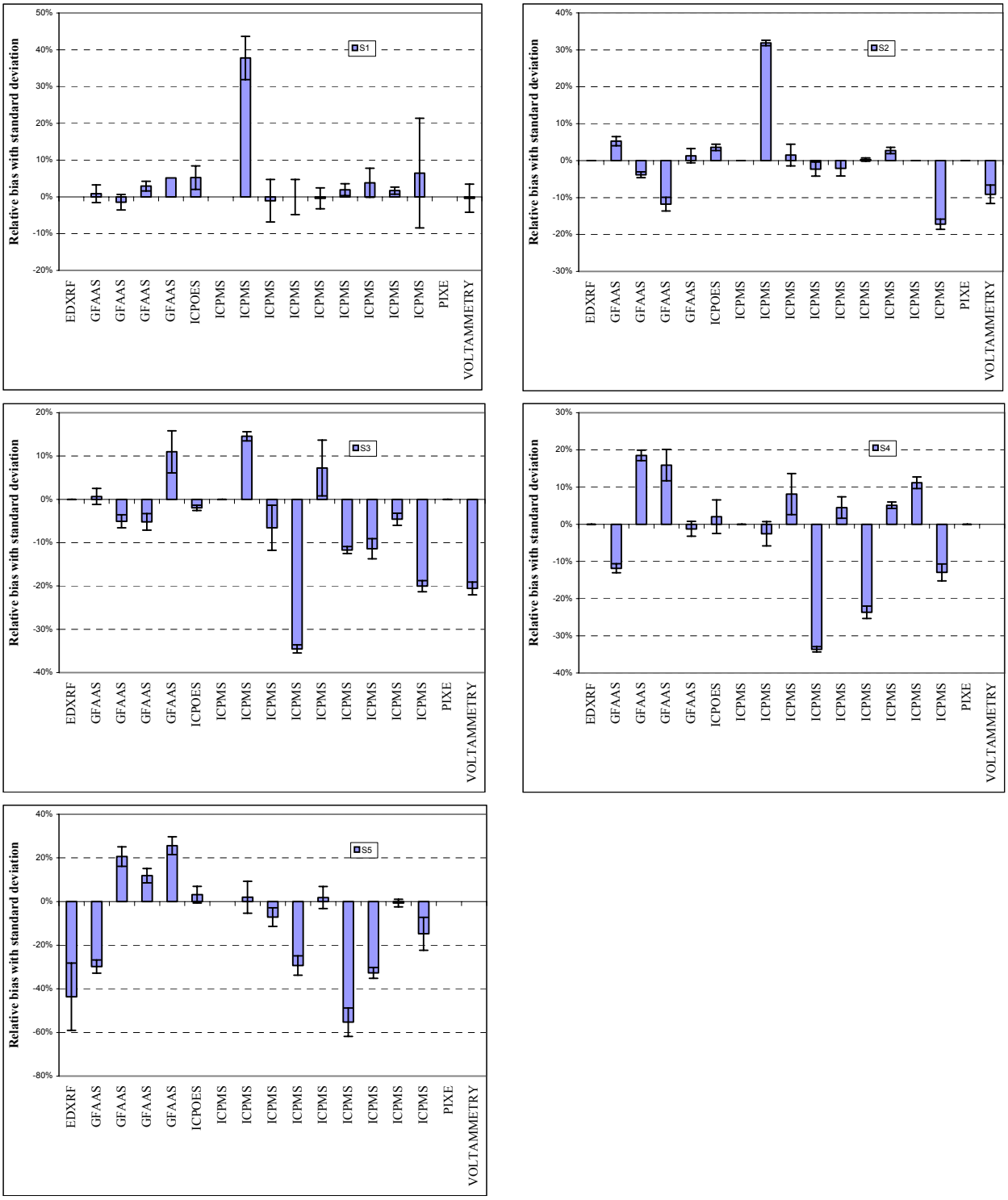


**Figure 16: Relative bias between reference values of test samples and NRL values grouped by measuring methods for Cd**

*The reference values were known to the laboratory using Voltammetry for $S_1$, $S_2$ and $S_3$.*

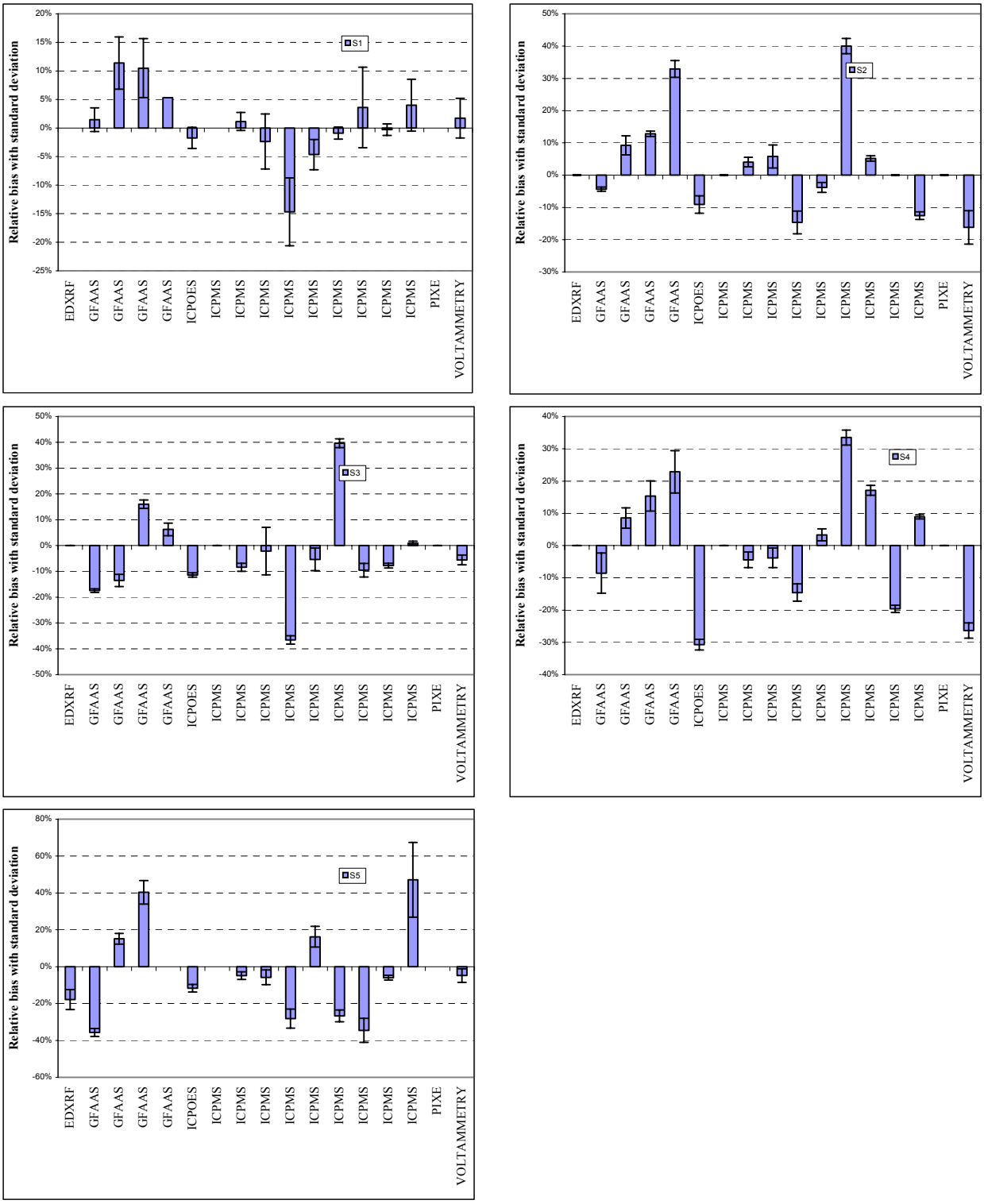


**Figure 17: Relative bias between reference values of test samples and NRL values grouped by measuring methods for Ni**

*The reference values were known to the laboratory using Voltammetry for $S_1$, $S_2$ and $S_3$.*

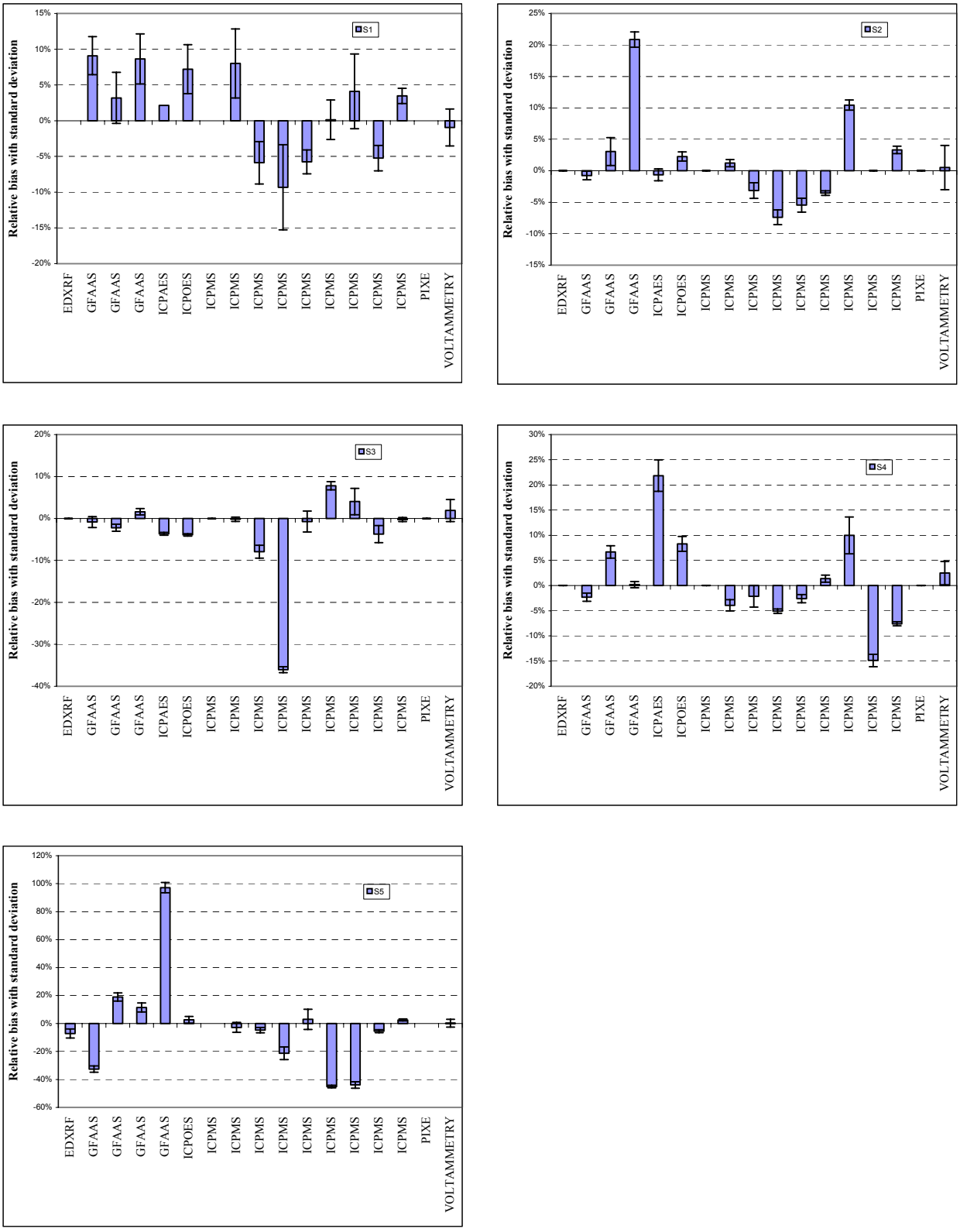


**Figure 18: Relative bias between reference values of test samples and NRL values grouped by measuring methods for Pb**

*The reference values were known to the laboratory using Voltammetry for $S_1$, $S_2$ and $S_3$.*

# Discussion and conclusion

Regarding the data quality objectives of the Daughter Directives, the best results were obtained for sample $S_3$, the CRM dust sample of NIST, for which 96 % of **z'score** was found satisfactory. On the opposite the worse results were obtained for $S_5$, the filter sample digested by participants for whom only 76 % of z'score were found satisfactory. With this observation, it is doubtful that an intercomparison exercise based only on the analysis of a CRM of dust may give a correct assessment of the quality of heavy metal determinations. Good results were also attained with liquid CRM, sample $S_1$, 92 % of z'score being satisfactory and thus suggesting that calibration may not be the main problem for $S_5$. Good results were also attained with $S_4$, the filters digested by JRC, with 93 % of z'score found satisfactory. This latter finding shows that if the same digestion (digestion performed by only one laboratory) is carried out on a set of identical filters then the results of analysis performed by all participants improve.

Regarding the DQO for $S_5$, nearly 85 % of z'score were satisfactory for Cd and Ni while this figures decreases to 64 and 73 % for As and Pb, respectively. For As and Pb, 22 and 20 % of z'score were found unsatisfactory, and strong outliers were observed. Except for As, the z'score for the liquid CRM ($S_1$) were at 92-100% satisfactory indicating that in general differences are not caused by direct calibration problem. This conclusion does not apply to As for which only 77 % of z'score were found satisfactory. Surprisingly, the z'score for $S_2$, $S_3$ and $S_4$ for As remained between 83 and 100 % thus higher values than for $S_1$ and $S_5$. This indicates that the source of faulty analysis on $S_5$ could be the digestion of filters.

In fact, some participants gave explanation for difficulties they encountered with the digestion of sample $S_5$. NRL1 and NRL12 observed an explosion in the microwave oven during the digestion of sample $S_5$. Nevertheless, they analysed what was left in the digestion vessel. Both of them gave results that were lower than the assigned value (one third of the assigned value for As, two third for Cd and Ni and half to two third for Pb). This discrepancy is likely to be caused by the explosions in the microwave and an incomplete digestion. One of these explosions could be explained by the lack of temperature regulation in the digestion vessel containing the filter. For the other explosion, the microwave digestion and the digestion program advised by EN 14902 is to be questioned. It is assumed that for As, Cd, Ni and Pb it would not be necessary to raise the temperature in the oven up to 200 ºC and that 180 ºC should be sufficient. On the other hand satisfactory results were obtained using other digestion methods: e. g. Soxhlet extraction, high pressure method and cold hydrogen fluoride method.
NRL10 reported a mistake on the dilution factor with which As, Cd, Ni and Pb for $S_5$ were multiplied: the values of NRL10 should have been the double of what was reported. By using this coefficient of dilution their z'score for As would have been: 0.1 for As (instead of -2.5), 0.5 for Cd (instead of -2.7), 2.2 for Ni (instead of -1.3) and 0.8 for Pb (instead of -3.8).

To explain the differences between their results and the reference values, NRL 7 emphasized that the acidity of the $S_1$, $S_2$ and $S_4$ samples prepared by JRC and their laboratory practice were diverse. NRL 7 normally prepares all their standards, reference materials and real samples with a $HNO_3$ of 3 %. The presence of HF in sample $S_2$ thus modifying the sample matrix was raised as a potential source of

interference. Moreover, the small amount of dust used to prepare the $S_3$ samples (when compared to the recommendations of NIST of 100 mg) could be a cause of lack of homogeneity of these samples. As the majority of participants found correct values for sample $S_3$ this last point may be groundless. NRL7 also reported not to have subtracted their laboratory blank for $S_1$ and $S_2$. However, the software of their instrument (Thermo ICP-MS software PlasmaLab) extracts automatically the calibration blanks in all samples, the calibration curve being forced through this blank. This means that the signal of $HNO_3$ 3% was subtracted from the signal of the samples. However, subtracting the blank to NRL7 would not have improved their results for all the elements. NRL 3, 8 and 10 did not subtract the blank either but the value of their blank was so small that it could be neglected.

NRL11 which had very high values for the $S_5$ filter on Ni and Pb reported very high blank for these elements. Nothing special was observed with the $S_5$-blank of the other participants (NRL1, 10 and 12). NRL3, which had high values for the $S_1$-$S_3$ samples, had no troubles with their laboratory and filter blanks.

Participants claimed uncertainties that were consistent with the DQO of the Directives (less than 25 % for Pb and less than 40 % for As, Cd and Ni). However the level of their claimed uncertainty was very scattered with the highest values being 6 to 7 times higher than the smallest one on $S_5$. More than half of the participants that reported uncertainty did not make a specific evaluation according to the type of sample ($S_1$ to $S_5$). About 75 % of the **En** numbers were between -1 and 1 showing a correct estimation of uncertainty of measurements. The majority of high En numbers for $S_5$ were caused by NRLs 1, 7, 11, 12 and 15. For NRL 1 and 12 we already said that the filter suffered an explosion during digestion. For NRL 15, a major interference was found out when analysing Cd by Voltammetry.

Regarding the comparability of measurements of heavy metals, the **reproducibility** given in Table 7 gives values that are extremely high: from 100 % for Pb to 200 % for As and Cd to 600 % for Nickel on the filter analysis $S_5$. However these high values are dominated by the strong outliers that were already noted for the z'score. The reproducibility figures decrease to values consistent with the DQO if these outliers are discarded taking into consideration that reproducibility should be compared to $\sqrt{2}$ DQOs. The **repeatability** remains between 5 and 12 % without much difference according to the sample type. Only the analysis of As on filter gives a repeatability that increases to 20 %.

These values should be compared with the repeatability/reproducibility of each participant calculated for analysis performed on different days and with different calibrations. The between-day variability is, in average, 8 % higher than the within-day variability both for samples $S_1$ and $S_5$.This suggests that by improving the quality control at laboratory level, the reproducibility could be decreased. In average, the most precise determinations are the ones of Pb (r = 3 % and R = 8 %) then Cd and Ni (r = 5 % and R = 12 %) and As (r = 10 % and R = 21 %). As is again the least precise determination as for z-score. Only small differences are observed between the liquid CRM $S_1$ and the filter sample $S_5$. It is important to note that the laboratory internal variability was not taken into account in the calculation of z'score and En numbers which used averages of set of 6 analysis and not individual measurements.

Regarding the influence of the different analytical methods on the quality of measurements, it can be noted that EDXRF had a limit of detection that was too high for carrying out accurate As analysis. This method also presented the highest within-

days and between-days variability for As and Cd (reproducibility up to 50 % for As and 60 % for Cd). Voltammetry showed a huge interference for the determination of Cd. The determination of As with this method is time consuming so that NRL15 did not report results for sample $S_5$. Good results were obtained using ICP-OES for Cd, Ni and Pb. For GF-AAS and ICP-MS, the two reference methods of analysis defined by the 4$^{th}$ Daughter Directive and EN 14902, a few high biases were also registered. They were associated with the explosions due to overpressure in the microwave oven, wrong dilution factor, contamination, high limit of detection, interference, acidity problem mentioned before.

# Annex 1: Cleaning of glass and PFA flasks

All labware (volumetric flasks, PFA vials, etc) was thoroughly cleaned before use according to the following procedure:

1. soak labware in nitric acid 10%, at least overnight; and preferably for several days;
2. rinse three times with nitric acid 10%;
3. rinse at least three times with MilliQ water;*
4. dry (at temperature below 50 °C) and store in a dust protected area.

*The digestion vessel of the microwave oven (Millestone Ethos) was further placed in an oven at 150 °C for two hours to improve the cleaning process.

# Annex 2: Certificates of analysis for $HNO_3$, $H_2O_2$ and HF

J. T. BAKER

A Division of Mallinckrodt Baker, Inc.
222 Red School Lane, Phillipsburg, NJ 08865
Phone: 908-859-2151 Fax: 908-859-9318
ISO 9000 Certified at ALL Facilities World-wide

CERTIFICATE OF ANALYSIS

Product No. 6901

Lot Number: B08416
Release Date: 1/5/2005

Nitric Acid
ULTREX®II Ultrapure Reagent

Formula $HNO_3$ F.W. 63.01

| TEST | SPECIFICATION | | RESULT |
|---|---|---|---|
| Assay (HNO3, w/w) | 67 - 70 % | | 70% |
| Trace Impurities in ppt (pg/g) | | | |
| Aluminum (Al) | 20 | max. | <10 |
| Antimony (Sb) | 10 | max. | <10 |
| Arsenic (As) | 20 | max. | <10 |
| Barium (Ba) | 10 | max. | <1 |
| Beryllium (Be) | 10 | max. | <5 |
| Bismuth (Bi) | 10 | max. | <0.1 |
| Boron (B) | 20 | max. | <10 |
| Cadmium (Cd) | 10 | max. | <1 |
| Calcium (Ca) | 20 | max. | <10 |
| Cerium (Ce) | 10 | max. | <0.05 |
| Cesium (Cs) | 10 | max. | <0.05 |
| Chromium (Cr) | 20 | max. | <10 |
| Cobalt (Co) | 10 | max. | <1 |
| Copper (Cu) | 20 | max. | <3 |
| Dysprosium (Dy) | 1 | max. | <0.01 |
| Erbium (Er) | 1 | max. | <0.01 |
| Europium (Eu) | 1 | max. | <0.01 |
| Gadolinium (Gd) | 1 | max. | <0.01 |
| Gallium (Ga) | 10 | max. | <1 |
| Germanium (Ge) | 10 | max. | <1 |
| Gold (Au) | 20 | max. | <10 |
| Hafnium (Hf) | 10 | max. | <0.05 |
| Holmium (Ho) | 1 | max. | <0.01 |
| Indium (In) | 1 | max. | <1 |
| Iron (Fe) | 20 | max. | <10 |
| Lanthanum (La) | 1 | max. | <0.05 |
| Lead (Pb) | 10 | max. | <1 |
| Lithium (Li) | 10 | max. | <1 |
| Lutetium (Lu) | 1 | max. | <0.01 |
| Magnesium (Mg) | 10 | max. | <5 |
| Manganese (Mn) | 10 | max. | <2 |
| Mercury (Hg) | 100 | max. | <100 |

CERTIFICATE OF ANALYSIS

Product No. 6901

Lot Number: B08416
Release Date: 1/5/2005

Nitric Acid
ULTREX®II Ultrapure Reagent

Formula $HNO_3$ F.W. 63.01

| Trace Impurities in ppt (pg/g) | | | |
|---|---|---|---|
| Molybdenum (Mo) | 10 | max. | <1 |
| Neodymium (Nd) | 1 | max. | <0.05 |
| Nickel (Ni) | 50 | max. | <10 |
| Niobium (Nb) | 1 | max. | <1 |
| Palladium (Pd) | 20 | max. | <10 |
| Platinum (Pt) | 20 | max. | <1 |
| Potassium (K) | 10 | max. | <5 |
| Praseodymium (Pr) | 1 | max. | <0.05 |
| Rhenium (Re) | 10 | max. | <1 |
| Rhodium (Rh) | 10 | max. | <1 |
| Rubidium (Rb) | 10 | max. | <1 |
| Ruthenium (Ru) | 20 | max. | <10 |
| Samarium (Sm) | 1 | max. | <0.01 |
| Scandium (Sc) | 10 | max. | <1 |
| Selenium (Se) | Information Only | max. | <20 |
| Silver (Ag) | 10 | max. | <2 |
| Sodium (Na) | 10 | max. | <5 |
| Strontium (Sr) | 10 | max. | <1 |
| Tantalum (Ta) | Information Only | max. | <10 |
| Tellurium (Te) | 1 | max. | <1 |
| Terbium (Tb) | 1 | max. | <0.01 |
| Thallium (Tl) | 10 | max. | <0.1 |
| Thorium (Th) | 1 | max. | <0.05 |
| Thulium (Tm) | 1 | max. | <0.01 |
| Tin (Sn) | 20 | max. | <10 |
| Titanium (Ti) | 10 | max. | <10 |
| Tungsten (W) | 10 | max. | <5 |
| Uranium (U) | 1 | max. | <0.01 |
| Vanadium (V) | 10 | max. | <1 |
| Ytterbium (Yb) | 1 | max. | <0.01 |
| Yttrium (Y) | 1 | max. | <1 |
| Zinc (Zn) | 20 | max. | <5 |
| Zirconium (Zr) | 10 | max. | <1 |

Marcy M Matlosz

Marcy M. Matlosz
Director of Quality

NOTE: This product is intended for laboratory and manufacturing use only. This product is not intended for drug, food or household use.
Regarding Food and Drug Administration (FDA) Regulations:

Ultimate Manufacurer and Supplier: SEASTAR CHEMICALS INC.
Street Address of Manufacturing Location: 10005 McDonald Park Road
City, State, ZIP of Manufacturing Location: Sidney, BC V8L 3S8
Country of Manufacturing Location: Canada
Phone: (250) 655-5880
Fax: (250) 655-5888

Is this product producted according to cGMP? No
Does this product have a Drug Master File? No
*Does this product comply with the ICH standard for residual solvents? No
*Is this product partly or fully of animal origin? No
*Does the manufacturing process of this product involve any raw materials, source materials or reagents that are of animal origin? No

# Hydrogen Peroxide

30%

ULTREX II Ultrapure Reagent

---

| | |
|---|---|
| **NC code:** | 2847 00 000 |
| **1L.=** | 1.11 |
| **Cas number.** | 7722-84-1 |
| **Formula** | $H_2O_2$ |
| **M=** | 34.01 |
| **UN-nr.** | 2014 |
| **EINECS** | 231-765-0 |
| **EC-nr.** | 8 003 00 9 |

| **Meets ACS Ultratrace Specifications.** | |
|---|---|
| Assay | 25.0-35.0% |
| Appearance | passes test |
| Free acid (µeq/g) | max. 0.5 |
| **Trace Impurities (in ppm):** | |
| Ammonium ($NH_4$) | max. 5 |
| Chloride (Cl) | max. 1 |
| Nitrate ($NO_3$) | max. 2 |
| Phosphate ($PO_4$) | max. 2 |
| Sulfate ($SO_4$) | max. 5 |
| **Trace Impurities (in ppt):** | |
| Silver (Ag) | max. 50 |
| Aluminium (Al) | max. 100 |
| Arsenic (As) | max. 1000 |

| | |
|---|---|
| Boron (B) | max. 1000 |
| Barium (Ba) | max. 50 |
| Beryllium (Be) | max. 1000 |
| Bismuth (Bi) | max. 1000 |
| Calcium (Ca) | max. 100 |
| Cadmium (Cd) | max. 50 |
| Cobalt (Co) | max. 50 |
| Chromium (Cr) | max. 50 |
| Copper (Cu) | max. 50 |
| Iron (Fe) | max. 100 |
| Gallium (Ga) | max. 1000 |
| Mercury (Hg) | max. 1000 |
| Potassium (K) | max. 100 |
| Lithium (Li) | max. 50 |
| Magnesium (Mg) | max. 50 |
| Manganese (Mn) | max. 50 |
| Molybdenum (Mo) | max. 1000 |
| Sodium (Na) | max. 100 |
| Nickel (Ni) | max. 50 |
| Lead (Pb) | max. 100 |
| Antimony (Sb) | max. 1000 |
| Silicon (Si) | max. 5000 |
| Tin (Sn) | max. 50 |
| Strontium (Sr) | max. 50 |
| Titanium (Ti) | max. 1000 |
| Vanadium (V) | max. 1000 |
| Zinc (Zn) | max. 50 |
| Zirconium (Zr) | max. 1000 |

# Annex 3: Reference value and uncertainty for $S_1$, $S_2$, $S_3$, $S_4$, $S_5$ and analysis of $S_6$

## Sample $S_1$

*Reference value*

The reference value for $S_1$ is calculated out of the certified heavy metals concentrations ($C_{BY14}$ and $C_{R14}$) of CRMs (see Annex 5) and $V_{BY14}$ and $V_{R14}$ the volumes injected with the two different micropipettes. $V_{BY14}$ and $V_{R14}$ were chosen so that the test values would be as closed as possible to the target value of the European Directives. The volumes of CRMs, that were injected with the micropipettes, were gravimetrically determined using water. $S_1$ was calculated using Eq. 4 where $m_{0.1}$ and $m_{0.9}$ are the masses of water in the two micropipettes. $d_{water}$ is the density of water, which was previously gravimetrically determined. The last term in Eq. 4 and 5 (Blk) represents the trace of heavy metals in the MilliQ water, $HNO_3$ and in the different glass/PFA vessels. Even though the MilliQ water, and reagent used for digestion had concentration of heavy metals in the range 0.001 ng/ml, the blank values for As, Cd, Ni, Pb, Zn and Cu were analysed and found to be less than 3 % of the reference values. Consequently they were neglected in the calculation using Eq. 4 and 5. However the blank values were considered as a contribution to the uncertainty calculation (see Eq. 6 and 7).

The volumes of BY14 and R14 that were injected into the PFA vial using the micropipettes were also determined by weighing. These weights could be used for determining $S_1$ using an independent route of traceability according to Eq. 5 where $m_{BY14}$ and $m_{R14}$ are the mass of injected volumes of CRMs and $d_{BY14}/d_{R14}$ are the densities of the CRMs that had to be gravimetrically determined.

The reference values of $S_1$ are given in Table 2 for both the volumetric and gravimetric method. Both of their values agree within uncertainties. Therefore, the reference value was calculated as the average between the volumetric and gravimetric determinations. These reference values were further confirmed by voltammetric analysis of $S_1$ for Cd, Pb, and Cu (see Table 9). In fact, the relative bias between analysis and calculated values were up to 8 % a value well within the uncertainty of voltammetry.

$$S1_{\mu g/l} = \frac{m_{0.1_g} / d_{water\,g/l} \; C_{BY14_{\mu g/l}} + m_{0.9_g} / d_{water\,g/l} \; C_{R14_{\mu g/l}}}{V_{fl_l}} + Blk_{\mu g/l} \quad \text{Eq. 4}$$

$$S1_{\mu g/l} = \frac{m_{BY14_g} / d_{BY14\,g/l} \; C_{BY14_{\mu g/l}} + m_{R14_g} / d_{BY14\,g/l} \; C_{R14_{\mu g/l}}}{V_{fl_l}} + Blk_{\mu g/l} \quad \text{Eq. 5}$$

**Table 9 Determination of Cd, Pb and Cu of the S1, a liquid sample of CRM for heavy metals**

| *Sample name* | *Zn*, ng ml$^{-1}$* | *Cd, ng ml$^{-1}$* | *Pb, ng ml$^{-1}$* | *Cu, ng ml$^{-1}$* |
|---|---|---|---|---|
| $S_1$ sample1 | 77.5 | 4.8 | 49.3 | 30.9 |
| $S_1$ sample2 | 78.3 | 5.1 | 51.6 | 30.5 |
| $S_1$ sample3 | 88.7 | 5.0 | 50.7 | 29.7 |
| $S_1$ sample4 | 89.1 | 4.7 | 49.1 | 29.2 |
| $S_1$ sample5 | 80.5 | 4.6 | 48.1 | 28.5 |
| $S_1$ sample6 | 83.6 | 4.7 | 48.6 | 29.1 |
| Average | 83.0 | 4.8 | 49.6 | 29.7 |
| Target value | 70.4 | 5.01 | 50.1 | 27.6 |
| **Relative bias** | 18% | - 3% | - 1% | 8% |

** The incorrect value for Zn is caused by the decrease of the deposition potential during analysis in order to improve Cd value in this analysis*

*Uncertainty of reference value*

The uncertainty of the reference value was calculated according to the "Guide to the Expression of Uncertainty in Measurement"[20]. The contribution of each component is calculated according to Eq. 6 and 7 obtained by applying the law of propagation of errors to Eq. 4 and 5. The factors contributing to the uncertainty are:

- for $u_{m0.1}$ and $u_{m0.9}$ and $d_{water}$: the repeatability of the weighing of water volumes in the pipettes and the uncertainty of the balance, the CRMs uncertainty for each heavy metals,
- for the flask: the maximum error of volume estimation by the manufacturer, the temperature expansion and reproducibility of filling.

The contributions due to the purity of reagents ($HNO_3$, MilliQ), 2-liter flask and PFA vial were quantified by analysing 6 samples of a solution of 10 ml of $HNO_3$ diluted with MilliQ water in a 2-liter flask. The expanded uncertainties of the metals of interest are given in Table 2. In the data treatment the determination based on the volumetric method was used. The gravimetric method gave the same reference values but with slightly higher uncertainties.

$$u_c^2(S_1) = \frac{C_{BY14}^2\, u^2(m_{0.1}) + C_{R14}^2\, u^2(m_{0.9}) + m_{0.1}^2\, u^2(C_{BY14}) + m_{0.9}^2\, u^2(C_{R14})}{(d_{water}\, V_{fl})^2} + \left(\frac{m_{0.1} C_{BY14} + m_{0.9} C_{R14}}{(-d_{water}\, V_{fl})^2}\right)^2 \left(\frac{u^2(d_{water})}{d_{water}^2} + \frac{u^2(V_{fl})}{V_{fl}^2}\right) + u^2(Blk) \quad \text{Eq. 6}$$

$$u_{S1}^2 = \left(\frac{C_{BY14}}{d_{BY14} V_{fl}}\right)^2 u^2(m_{BY14}) + \left(\frac{m_{BY14}}{d_{BY14} V_{fl}}\right)^2 u^2(C_{BY14}) + \left(\frac{m_{BY14} C_{BY14}}{d_{BY14}(-V_{fl})^2}\right)^2 u^2(V_{fl}) + \left(\frac{m_{BY14} C_{BY14}}{(-d_{BY14})^2 V_{fl}}\right)^2 u^2(d_{BY14}) + \left(\frac{C_{R14}}{d_{R14} V_{fl}}\right)^2 u^2(m_{BY14}) + \left(\frac{m_{R14}}{d_{R14} V_{fl}}\right)^2 u^2(C_{R14}) + \left(\frac{m_{R14} C_{R14}}{d_{R14}(-V_{fl})^2}\right)^2 u^2(V_{fl}) + \left(\frac{m_{R14} C_{R14}}{(-d_{R14})^2 V_{fl}}\right)^2 u^2(d_{R14}) + u^2(Blk) \quad \text{Eq. 7}$$

## Sample $S_2$

*Reference value*

The reference value of $S_2$ was calculated using Eq. 8 where m is the weighed mass of CRM, CRM is the certified heavy metal mass ratios of the NIST SRM 1648 (see Certificate of Analysis in Annex 6), V is the final dilution volume (glass flask of 1 litre) and k is the efficiency of digestion. The last term in Eq. 8 (Blk) represents the trace of heavy metals in the MilliQ water, in $HNO_3$, HF and $H_2O_2$ in the different glass/PFA vessels. Even though the MilliQ water, and reagent used for digestion had concentration of heavy metals in the range 0.001 ng/ml, the blank values for As, Cd, Ni, Pb, Zn and Cu were analysed and found to be less than 1 % of the reference values. Consequently they were neglected in the calculation using Eq. 8. However the blank values and its standard deviation were considered as a contribution to the uncertainty calculation (see Eq. 9).

[20] "Guide to the Expression of Uncertainty in Measurement published by the International Standard Organisation (ISO) in 1995

In Eq. 8, the efficiency of the digestion, as carried out by JRC is necessary. The best estimation of this efficiency was the average of the ratios of NRLs values and reference value for $S_2$ out of the same ratio for $S_1$ (characteristic of the calibration skill of each NRL), the outliers (applying the Grubb's test for the "one small" and "one low" values) being discarded. As for the blank value, the digestion was set to 1 but was considered as a contribution to the uncertainty calculation

$$S2_{ng/ml} = k\frac{m_g\, CRM_{\mu g/g}}{V_l} + Blk_{ng/ml} \quad \text{Eq. 8}$$

**Table 10: Mean ratios of NRLs results out of reference values for $S_1$-$S_4$ for several elements.**

| Samples, Elements | As | $s_{As}$ | Cd | $s_{Cd}$ | Ni | $s_{Ni}$ | Pb | $s_{Pb}$ | Zn | $s_{Zn}$ | Cu | $s_{Cu}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $S_1$ ratio | 1.04 | 0.08 | 1.05 | 0.11 | 1.01 | 0.07 | 1.00 | 0.06 | 1.11 | 0.09 | 1.01 | 0.06 |
| $S_2$ ratio | 1.17 | 0.13 | 1.04 | 0.10 | 1.07 | 0.17 | 1.00 | 0.05 | 1.02 | 0.07 | 0.95 | 0.06 |
| $S_3$ ratio | 1.03 | 0.13 | 0.99 | 0.09 | 0.95 | 0.10 | 0.96 | 0.11 | - | - | - | - |
| $S_4$ ratio | 1.05 | 0.24 | 0.98 | 0.15 | 1.00 | 0.19 | 1.01 | 0.09 | - | - | - | - |
| $S_3/S_2$* | 0.92 | 0.10 | 0.96 | 0.09 | 0.93 | 0.10 | 0.98 | 0.06 | 0.95 | 0.06 | 0.95 | 0.04 |
| $S_2/S_1$+ | 1.12 | 0.06 | 0.99 | 0.03 | 0.98 | 0.07 | 0.99 | 0.04 | 0.96 | 0.06 | 0.95 | 0.03 |

+*The efficiency of digestion for $S_2$ carried out by JRC is estimated by the $S_2/S_1$ ratio.*
**The mean efficiency of the digestion carried out by NRL is estimated by the $S_3/S_2$ ratio*

The reference values for each heavy metal in $S_2$ are given in Table 2. These reference values were further confirmed by voltammetric analysis of $S_2$ for Zn, Cd, Pb, and Cu (see Table 11). In fact, the relative bias between analysis and calculated values were up to 6 % a value well within the uncertainty of voltammetry.

**Table 11 Confirmation by analysis of the calculated value of $S_2$ for Zn, Cd, Pb and Cu**

| Sample name | Zn, ng ml$^{-1}$ | Cd, ng ml$^{-1}$ | Pb, ng ml$^{-1}$ | Cu, ng ml$^{-1}$ |
|---|---|---|---|---|
| S2 sample1 | 699 | 10.8 | 1017 | 94.3 |
| S2 sample2 | 698 | 10.8 | 1001 | 91.9 |
| S2 sample3 | 725 | 10.8 | 1027 | 93.8 |
| S2 sample4 | 723 | 10.6 | 1000 | 91.1 |
| S2 sample5 | 723 | 10.6 | 996 | 90.8 |
| S2 sample6 | 727 | 10.7 | 1011 | 91.7 |
| Average | 716 | 10.7 | 1009 | 92.3 |
| Target value | 724 | 11.4 | 996 | 92.6 |
| Relative bias | 1.1 % | 6 % | 1.3 % | 0.3 % |

*Uncertainty of reference value*

The uncertainty of the $S_2$ is calculated according to the Eq. 9. The factors contributing to the uncertainty of $S_2$ are: the uncertainty of each mass ratio found in the NIST certificate (see Annex 6), the uncertainty of weighing the NIST 1648, the uncertainty of digestion (see Table 10), the uncertainty of the flask volume and the uncertainty of the blank value. The blank value was estimated by the quadratic sum of the average of 6 analyses of reagent blank and its standard deviation. The expanded uncertainties of the metals of interest are given in Table 2.

$$u^2(S_2) = \left(\frac{k\,CRM}{V}\right)^2 u^2(m) + \left(\frac{k\,m}{V}\right)^2 u^2(CRM) + \left(\frac{m\,CRM}{V}\right)^2 u^2(k) + \left(k\frac{m\,CRM}{(-V)^2}\right)^2 u^2(V) + u^2(Blk) \quad \text{Eq. 9}$$

## Sample $S_3$

In order to ease the data treatment and to refer to the certified mass ratio of the NIST certificate, the mass of $S_3$ determined by each participant for each heavy metal was

divided by the mass of CRM in the vial determined by weighing at the JRC (see Table 12).

**Table 12 Masses of dust weighed by JRC and sent to all NRLs with their standard uncertainties**

| NRLs | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m in g | 0.01341 | 0.01470 | 0.00769 | 0.01172 | 0.01023 | 0.01422 | 0.01065 | 0.00973 | 0.01367 | 0.01102 | 0.00952 | 0.00934 | 0.01189 | 0.01103 | 0.00765 |
| u(m) in g | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 | 0.00012 |

*Reference value*

The reference mass ratios to be used for $S_3$ are the ones given in the NIST certificate (see Annex 6). It was also verified by analysis that the mass of heavy metals in the PFA vial after cleaning were small enough to be neglected.
The recovery of 6 of the $S_3$ samples was determined by voltammetric analysis. The results are presented in Table 13. The differences between analyses and NIST certified values were well within the uncertainty of voltammetry and certified values apart for Cd for which the level of concentration was too low compared to the detection limit of voltammetry for Cd. Nevertheless, considering the preparation method for $S_3$, it is quite unlikely that a negative bias may have occurred only for Cd and not for Zn, Pb and Cu and thus all the other elements.

**Table 13 Confirmation of the reference values by analysis of 6 test samples $S_3$**

| | | Analysis mg/kg | target mg/kg | Recovery % |
|---|---|---|---|---|
| S3_4 | Zn | 4669 | 4760 | 98% |
| | Cd | 61 | 75 | 82% |
| | Pb | 6717 | 6550 | 103% |
| | Cu | 597 | 609 | 98% |
| S3_7 | Zn | 4434 | 4760 | 93% |
| | Cd | 61 | 75 | 81% |
| | Pb | 6591 | 6550 | 101% |
| | Cu | 573 | 609 | 94% |
| S3_13 | Zn | 4544 | 4760 | 95% |
| | Cd | 59 | 75 | 78% |
| | Pb | 6511 | 6550 | 99% |
| | Cu | 552 | 609 | 91% |
| S3_15 | Zn | 4602 | 4760 | 97% |
| | Cd | 59 | 75 | 78% |
| | Pb | 6591 | 6550 | 101% |
| | Cu | 546 | 609 | 90% |
| S3_16 | Zn | 4552 | 4760 | 96% |
| | Cd | 65 | 75 | 87% |
| | Pb | 6911 | 6550 | 106% |
| | Cu | 585 | 609 | 96% |
| S3_21 | Zn | 4652 | 4760 | 98% |
| | Cd | 62 | 75 | 83% |
| | Pb | 6850 | 6550 | 105% |
| | Cu | 578 | 609 | 95% |

*Reported values of NRLs*

It was shown by analysis that the mass of heavy metals in the PFA vial after cleaning according to the EN 14902 procedure could be neglected. For each NRL, the mass

ratios were calculated by dividing the mass of each heavy metal determined by a NRL with the mass of the sample dust of NIST 1648 introduced in each used vial by JRC and calculated according to Eq. 10 where $m_{HM}$ is the mass of heavy metal determined by each NRL and m is the mass of dust weighed by JRC.

$$S_{3\,ng/mg} = \frac{m_{HM_{ng}}}{m_{mg}} \quad \text{Eq. 10}$$

To limit the uncertainty of the mass of NIST in the vial, a double weighing procedure was carried out. First, the empty vial was weighed on 2 different days after cleaning and stabilization to the ambient conditions of the balance room. Then the mass of NIST 1648 introduced in the open vial was weighed by difference. Two days after, the full closed vial was weighed again. The difference between the full and empty vial could be compared with the direct weight of NIST 1648 introduce in the vial.
Then, the uncertainty of $S_3$ claimed by each NRL shall be recalculated using Eq. 11 which is derived from Eq. 10. In this equation, the uncertainty of the weighing estimated by JRC ($u_m$) is added to the uncertainty of the NRLs ($u(m_{HM})$). Table 12 gives m, the mass of sample $S_3$ and its standard uncertainty for all NRLs. It can be observed that the $u_m$ is less than 1.6 % of m compared to the NRL's uncertainty.

$$u_c^2(S_3) = \frac{u^2(m_{HM})}{m^2} + \left(\frac{m_{HM}}{m}\right)^2 \frac{u^2(m)}{m^2} = \left(\frac{u(m_{HM})}{m}\right)^2 + \left(S_3 \frac{u(m)}{m}\right)^2 \quad \text{Eq. 11}$$

*Uncertainty of reference value*

The uncertainty of the reference mass ratios are also given in NIST certificate (see Annex 6).

## Robust means and standard deviations for test samples $S_4$ and $S_5$

For the exposed filters $S_4$ and $S_5$ no certified values were available. The assigned values and their uncertainty could not be known before the IE. Therefore the assigned values and their uncertainty were based on consensus values from all participants following the algorithm given in annex C of ISO 13528[21]. However, obvious irregularities and reported incidents (see Annex 9: Scrutiny of results for consistency and statistical outliers) during analysis were discarded before determining the robust means in order to avoid bias from erroneous methods. The algorithm yields robust values of the average and standard deviation of the data to which it is applied. The calculation has been done averaging all measurement of $S_5$. The standard uncertainty of the assigned values was calculated using the equation (8) where s* is the robust standard deviation of the robust mean calculated according to the algorithm A of ISO 13528 and p are the number of laboratories. The robust mean and standard uncertainties of the metals of interest are given in Table 4.

$$u_X = 1.25\, s^* \Big/ \sqrt{p} \quad \text{Eq. 12}$$

The robust estimates x* and s* may be derived by an iterative calculation, i.e. by updating the values of x* and s* several times using the modified data, until the process converges. Convergence may be assumed when there is no change from one iteration to the next in the third significant figure of the robust standard deviation and

[21] *ISO 13528:2005, Statistical methods for use in proficiency testing by interlaboratory comparisons, Geneva, CH.*

of the equivalent figure in the robust average. This is a simple method to program on a computer.

## Sample $S_6$

A subsequent set of samples outside the scope of the IE was prepared for a limited number of NRLs which asked to have the possibility to test different digestion or analytical methods on filters sampled at the same site and on the same day.

**Table 14 Means and standard deviation of sample $S_6$ in ng**

| Laboratory | Filter no | As | | Cd | | Ni | | Pb | |
|---|---|---|---|---|---|---|---|---|---|
| | | mean | s | mean | s | mean | s | mean | s |
| NRL 8 | 1 | - | - | 33.1 | 2.9 | 180.9 | 7.9 | 1723.0 | 49.3 |
| | 2 | - | - | 32.9 | 1.1 | 180.5 | 16.5 | 1726.1 | 34.3 |
| | 3 | - | - | 34.7 | 2.5 | 194.5 | 15.2 | 1808.9 | 34.7 |
| | 4 | - | - | 33.7 | 2.4 | 174.0 | 17.4 | 1743.1 | 50.6 |
| NRL 12 | 1 | 23.8 | 1.8 | 21.9 | 1.3 | 213.6 | 11.0 | 1321.0 | 34.5 |
| | 2* | 96.8 | 4.4 | 52.2 | 1.0 | 479.0 | 28.6 | 2071.6 | 40.5 |
| NRL 15 | 1 | - | - | - | - | 322.9 | 22.5 | 1722.1 | 19.2 |
| | 2 | - | - | - | - | 328.4 | 11.7 | 1763.3 | 49.0 |
| | 3* | - | - | - | - | 352.7 | - | 2010.0 | 29.4 |
| | 4* | - | - | - | - | 360.5 | - | 1938.2 | 63.2 |

**** digestion using dissolution with HF and $HNO_3$ method (Jalkanen, L.M. and Häsänen, E.K., J. Anal. At. Spectrom., 1996, Vol. 11, 365-369, .while the other filters were digested using EN 14902 method (microwave)***

# Annex 4: Digestion procedure

A microwave system 'ETHOS TOUCH' was used in this intercomparison. The temperature controlled digestion procedure consisted of 1) twenty minutes of linearly increasing temperature between ambient and 220 ºC, 2) twenty five minutes of constant temperature (220 ºC) with a maximum power in the vessels of 800 W and 3) twenty minutes of cooling. This process was repeated once in order to be sure that the entire mass of dust is digested. Afterwards, the digestion vessel was opened in small steps over one hour so that the pressure was released slowly avoiding evaporation or liquid lost by spraying of small droplets.

# Annex 5: Certificates of calibration of R14 and BY14

ROMIL CERTIFICATION!

PURE CHEMISTRY

PrimAg®

UKAS CALIBRATION 0658

ISO 17025

## Certificate of Calibration

Certificate Number: P549465
Date Issued: 21/09/2006
Page 1 of 1 pages

**Description:** **ICP Calibration mix BY14**

**multi-element reference solution**

**Category & Code:** *ROMIL PrimAg®-plus* *ME794*

**Specification:**

14 components:
Mn, Zn 500 ppm each
Co, Cr, Cu, Ni, Pb, V 100 ppm each
As, Mo, Sb, Se, Sn 50 ppm each
Cd 10 ppm
Matrix: HNO3 0.5M/HCl 2M
Application: ICP calibration

**Batch Number:** P549465
**Date of Calibration:** September 2006

| Component: | Calibration Result (m/v @ 20°C): | Expanded Uncertainty: |
|---|---|---|
| Mn | 500 ppm | ±1 ppm |
| Zn | 500 ppm | ±1 ppm |
| Co | 100.0 ppm | ±0.4 ppm |
| Cr | 100.2 ppm | ±0.3 ppm |
| Cu | 100.0 ppm | ±0.2 ppm |
| Ni | 100.0 ppm | ±0.3 ppm |
| Pb | 100.0 ppm | ±0.2 ppm |
| V | 100.0 ppm | ±0.3 ppm |
| As | 50.0 ppm | ±0.1 ppm |
| Mo | 50.0 ppm | ±0.2 ppm |
| Sb | 50.0 ppm | ±0.2 ppm |
| Se | 50.0 ppm | ±0.2 ppm |
| Sn | 50.0 ppm | ±0.1 ppm |
| Cd | 10.00 ppm | ±0.03 ppm |

**Approved Signatory:**
**Dr Robert M Lenk**
**CChem MRSC**

Printed from a master computer file which has been authorised by the signatory.

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

This certificate is issued in accordance with the laboratory accreditation requirements to ISO 17025 of the United Kingdom Accreditation Service (UKAS). It provides SI-traceability of measurement to the mole realised by a PrimAg primary silver reference material, also to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. UKAS is one of the signatories to the Multilateral Agreement of the European co-operation for Accreditation (EA) as well as the International Laboratory Accreditation Cooperation (ILAC) Arrangement for the mutual recognition of calibration certificates issued by accredited laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of ROMIL Ltd. PrimAg is a registered trademark of ROMIL Ltd.

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ROMIL CERTIFICATION!

PURE CHEMISTRY

# Certificate of Calibration

Certificate Number: E557465
Date Issued: 02/10/2006


0658 ISO 17025

**Description:** **ICP Calibration mix R14**

**multi-element reference solution**

**Category & Code:** *ROMIL PrimAg®-plus* *ME184*

**Specification:**

14 components:
Al 2500 ppm
Fe 2000 ppm
Mn, Pb, Zn 100 ppm each
Cr, Cu, Ni, V 50 ppm each
As, Cd, Co, Hg, Mo 10 ppm each
Matrix: HNO3 0.5M/HCl 0.1M
Application: ICP calibration

**Batch Number:** E557465
**Date of Calibration:** September 2006

| Component: | Calibration Result (m/v @ 20°C): | Expanded Uncertainty: |
|---|---|---|
| Al | 2504 ppm | ±4 ppm |
| Fe | 1999 ppm | ±4 ppm |
| Mn | 100.0 ppm | ±0.2 ppm |
| Pb | 100.0 ppm | ±0.4 ppm |
| Zn | 100.0 ppm | ±0.3 ppm |
| Cr | 49.74 ppm | ±0.11 ppm |
| Cu | 49.95 ppm | ±0.15 ppm |
| Ni | 49.98 ppm | ±0.13 ppm |
| V | 49.96 ppm | ±0.08 ppm |
| As | 10.00 ppm | ±0.03 ppm |
| Cd | 9.99 ppm | ±0.03 ppm |
| Co | 10.00 ppm | ±0.04 ppm |
| Hg | 10.00 ppm | ±0.02 ppm |
| Mo | 10.00 ppm | ±0.04 ppm |

**Approved Signatory:**
**Dr Robert M Lenk**
**CChem MRSC**

Printed from a master computer file which has been authorised by the signatory.

The reported expanded uncertainty is based on a standard uncertainty multiplied by a coverage factor $k = 2$, providing a level of confidence of approximately 95%. The uncertainty evaluation has been carried out in accordance with UKAS requirements.

This certificate is issued in accordance with the laboratory accreditation requirements to ISO 17025 of the United Kingdom Accreditation Service (UKAS). It provides SI-traceability of measurement to the mole realised by a PrimAg primary silver reference material, also to recognised national standards, and to units of measurement realised at the National Physical Laboratory or other recognised national standards laboratories. UKAS is one of the signatories to the Multilateral Agreement of the European co-operation for Accreditation (EA) as well as the International Laboratory Accreditation Cooperation (ILAC) Arrangement for the mutual recognition of calibration certificates issued by accredited laboratories. This certificate may not be reproduced other than in full, except with the prior written approval of ROMIL Ltd. PrimAg is a registered trademark of ROMIL Ltd.

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*1000ppm is equivalent to 1g per litre of the nominal component (ref Romil)*

# Annex 6: Certificate of analysis of NIST 1648

Table 1. Certified Values of Constituent Elements

Major Constituents

| Element | Content[a] Mass Fraction, in % |
|---|---|
| Aluminum[b] | 3.42 ± 0.11 |
| Iron | 3.91 ± 0.10 |
| Potassium[b] | 1.05 ± 0.01 |

Minor Constituents

| Element | Content[a] Mass Fraction, in % |
|---|---|
| Lead | 0.655 ± 0.008 |
| Sodium[b] | 0.425 ± 0.002 |
| Zinc | 0.476 ± 0.014 |

Trace Constituents

| Element | Content[a] mg/kg |
|---|---|
| Arsenic | 115 ± 10 |
| Cadmium | 75 ± 7 |
| Chromium | 403 ± 12 |
| Copper | 609 ± 27 |
| Manganese[c] | 786 ± 17 |

| Element | Content[a] mg/kg |
|---|---|
| Nickel | 82 ± 3 |
| Selenium[b] | 27 ± 1 |
| Uranium | 5.5 ± 0.1 |
| Vanadium[c] | 127 ± 7 |

[a] The uncertainties of the certified values, except those noted, include errors associated with both measurement and material variability. They represent the 95 % tolerance limits for individual subsamples, i.e., 95 % of the subsamples from a single unit of this SRM would be expected to have a composition within the indicated range of values 95 % of the time.

[b] The indicated constituent was certified as a part of the NIST update certification program, in August 1991. The value for each indicated constituent is the "best value" based on all measurement methods used and the associated uncertainty is expressed as the standard error considering variability within and between analytical methods.

[c] The uncertainty in the certified value is calculated as $U = ku_c + B$ where $u_c$ is the combined standard uncertainty calculated according to the ISO Guide [1] and $k$ is a coverage factor. The additional quantity, $B$, is an allowance for the differences between methods of analysis and is taken to be equal to the difference between the most discrepant method value and the certified value. The expanded uncertainty ($U$) given is intended to approximate the 95 % level of confidence.

# Annex 7: Homogeneity of sampling $PM_{10}$ with Low Volume Samplers

A first check of homogeneity was performed in Ispra (I) in order to evaluate the extent of deviation of $PM_{10}$ mass concentration and of selected heavy metals. Seventeen filters (Whatman quartz 47 mm) were weighed in the balance room of ERLAP. All the LVS's were exposed in the same time for 24 h having a flow of 55.2 $m^3$. The homogeneity was checked by gravimetry and voltammetry methods respectively. Further to this experiment, the RSD of the LVS method was estimated to be 4 % both for the mass concentration of $PM_{10}$ and the heavy metals. There is an exception for Cd but the level of this element was very low in the analysed filters. Furthermore, it was analysed using voltammetry which was shown to suffer from interference for the Cd analysis.

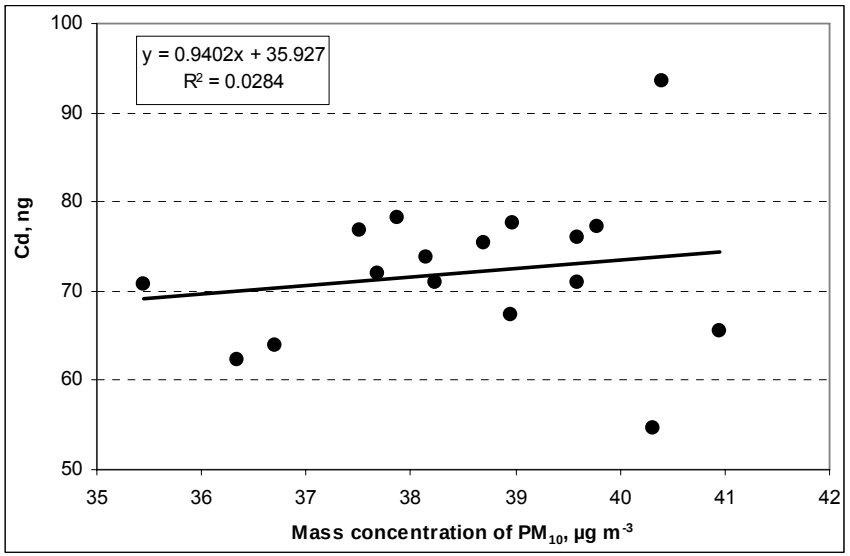
As shown in Figure 19, there is no obvious correlation between the $PM_{10}$ concentration and the level of heavy metals on filters. Therefore, there is no possibility to normalise the analysed heavy metals with the $PM_{10}$ mass concentration of a filter.

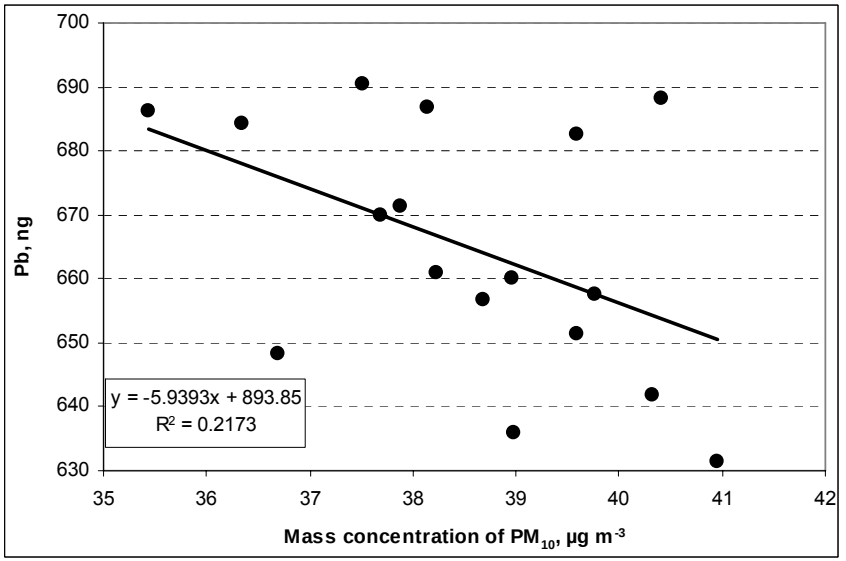
Seeing the good results of the homogeneity test, it was decided to start the real exposition for the intercomparison of heavy metals in $PM_{10}$. The LVS's were transported to Milan (I), to a monitoring station of ARPA Lombardia. The RSD of 4 % was confirmed for the mass concentration of PM10 during the intercomparison in Milan (see Table 16). If only the quartz filters are considered then the RSD further decreases to 3 % for $PM_{10}$ higher than 50 µg/m³ (see Figure 20)

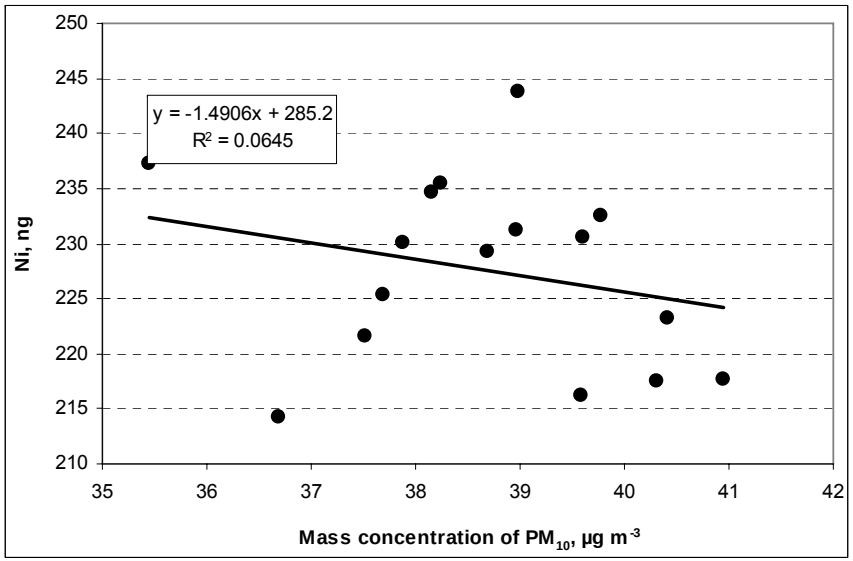
**Table 15 Evaluation of homogeneity of $PM_{10}$ mass concentration and heavy metals carried out in Ispra (I) before the intercomparison in Milan**

| Filter nr | Gravim., µg. $m^{-3}$ | Cd, ng. $ml^{-1}$ | Pb, ng. $ml^{-1}$ | Cu, ng. $ml^{-1}$ | Ni, ng. $ml^{-1}$ |
|---|---|---|---|---|---|
| 1 | 40.3 | 2.2 | 25.7 | 78.3 | 8.7 |
| 2 | 37.9 | 3.1 | 26.8 | 82.1 | 9.2 |
| 3 | 35.4 | 2.8 | 27.4 | 84.1 | 9.5 |
| 4 | 37.7 | 2.9 | 26.8 | 80.2 | 9.0 |
| 5 | 38.7 | 3.0 | 26.3 | 81.7 | 9.1 |
| 6 | 39.8 | 3.1 | 26.3 | 81.9 | 9.3 |
| 7 | 39.6 | 2.8 | 26.1 | 82.7 | 8.6 |
| 8 | 40.9 | 2.6 | 25.3 | 80.2 | 8.7 |
| 9 | 39.0 | 2.7 | 26.4 | 94.6 | 9.2 |
| 10 | 36.3 | 2.5 | 27.4 | 81.0 | 19.2* |
| 11 | 39.0 | 3.1 | 25.4 | 77.1 | 9.7 |
| 12 | 39.6 | 3.0 | 27.3 | 85.9 | 9.2 |
| 13 | 40.4 | 3.7 | 27.5 | 89.6 | 8.9 |
| 14 | 38.1 | 2.9 | 27.5 | 81.5 | 9.4 |
| 15 | 37.5 | 3.1 | 27.6 | 82.9 | 8.9 |
| 16 | 38.2 | 2.8 | 26.4 | 78.8 | 9.4 |
| 17 | 36.7 | 2.6 | 25.9 | 78.5 | 8.6 |
| Average | 38.5 | 2.9 | 26.6 | 82.4 | 9.1 |
| CV | 4% | 12% | 3% | 5% | 4% |

* outlier



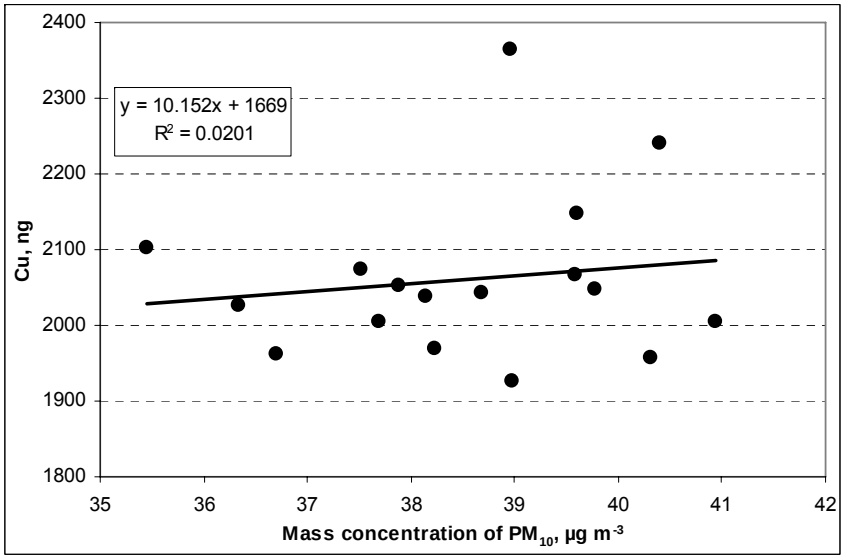




**Figure 19 Masses of Cd, Pb, Ni and Cu in the filter versus the mass concentrations of PM10 for 17 filters exposed simultaneously at the same site (Ispra)**

**Table 16: Evaluation of homogeneity of $PM_{10}$mass concentration in Milan for 16 LVS .**

| *Filter type and NRLs* | *S4 (13-14.12.06)* | *14-15.12.06* | *S5(19-20.12.06)* |
|---|---|---|---|
| Quartz 0, 1 | 118.4 | 195.4 | 55.4 |
| Quartz 2 | 117.9 | 195.6 | 55.8 |
| Quartz 3 | 114.0 | 186.5 | 54.2 |
| Quartz 4 | 115.8 | 193.9 | 53.8 |
| Quartz 5 | 118.5 | 196.5 | 55.9 |
| Quartz 6 | 121.4 | 203.4 | 57.2 |
| Quartz 7 | 116.8 | 195.7 | 56.0 |
| Quartz 8 | 115.5 | 195.9 | 55.4 |
| Quartz 9 | 118.0 | 175.1 | 58.1 |
| Quartz 10 | 120.2 | 195.1 | 56.5 |
| Quartz 11 | 115.7 | 191.4 | 55.3 |
| Quartz 12 | 118.9 | 185.2 | 55.5 |
| Pall 13 | 108.8 | 174.8 | 49.9 |
| Pall 14 | 108.8 | 180.6 | 52.8 |
| Quartz 15 | 113.3 | 185.7 | 53.5 |
| Quartz 16 | 115.7 | 188.9 | 55.1 |
| Quartz, µg/m³ | 117.2 | 191.7 | 55.6 |
| Pall, µg/m³ | 108.8 | 177.7 | 51.3 |
| RSD all filters, % | 3.1% | 4.3% | 3.5% |
| RSD without Pall filters, % | 2.0% | 2.7% | 2.3% |

*The row labelled "Quartz" and "Pall" compare the average of $PM_{10}$ mass concentration for the two types of filters. The last row gives the relative standard deviation for all filters..*

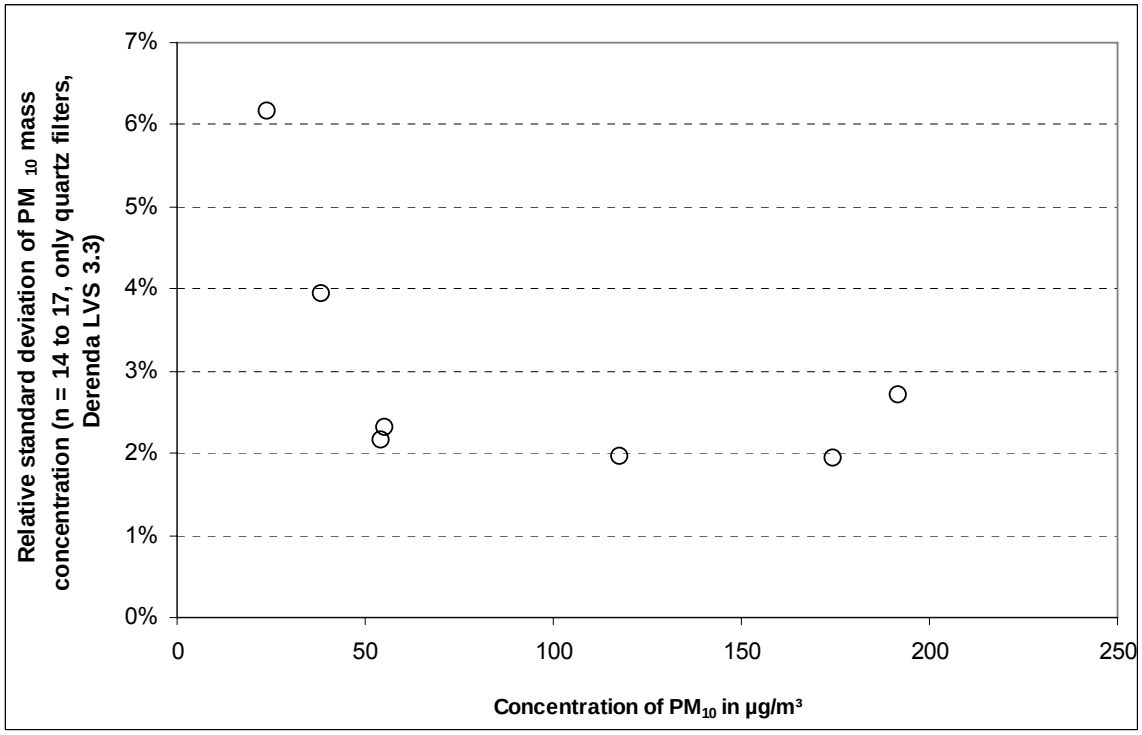



**Figure 20: Trend of RSD of mass concentration of $PM_{10}$ for simultaneous sampling with 14-17 LVSs using only quartz filters in Ispra and in Milan**

Annex 8: Results of the intercomparison exercise

**Table 17: Means of As for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 41.2$^{+}$ | 56.0$^{+}$ | 46.8$^{+}$ |
| 1 | 7.14 | 7.24 | 7.30 | 20.6 | 122 | 5.9 | 44.8$^{o}$ | 37.9$^{o}$ | 45.5$^{o}$ |
| 2 | | | | | | | | | |
| 3 | 9.50 | 9.83 | 10.52 | 24.5 | 142 | 4.5 | 118 | 124 | 135 |
| 4 | 6.99 | 7.08 | 7.02 | 19.4 | 113 | 5.7 | 109 | 114 | 113 |
| 5 | 7.66 | 7.36 | 7.45 | 20.5 | 122 | 6.7 | 159 | 150 | 147 |
| 6 | 6.29 | 6.64 | 6.39 | 19.0 | 113 | 4.6 | 106 | 126 | 104 |
| 7 | 8.44 | 8.95 | 8.03 | 25.3 | 82.5 | 4.4 | 119 | 116 | 107 |
| 8 | 6.84 | 7.40 | 8.12 | 19.7 | 133 | 9.0** | 147 | 144 | 147 |
| 9 | 6.96 | 7.28 | 7.14 | 18.0 | 132 | 5.4 | 123 | 119 | 138 |
| 10 | 8.45 | 7.57 | 8.58 | 23.6 | 117 | 4.6 | 60.3$^{x}$ | 61.9$^{x}$ | 61.9$^{x}$ |
| 11 | 7.27 | 6.92 | 7.07 | 19.1 | 119 | 4.9 | 352$^{+}$ | 335$^{+}$ | 353$^{+}$ |
| 12 | 6.82 | 7.22 | 7.40 | 19.0 | 107 | 5.2 | 28.5$^{o}$ | 40.1$^{o}$ | 39.2$^{o}$ |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 6.89 | 6.82 | 6.88 | | 112 | 4.6 | 124 | 107 | 113 |
| 15 | 7.82$^{-}$ | 7.77$^{-}$ | 6.65$^{-}$ | 17.9$^{-}$ | 119$^{-}$ | 5.4 | | | |
| 16 | 6.60 | 8.50 | 7.19 | 15.8 | 96.8 | 4.5 | 92.4 | 94.9 | 108 |

**Table 18: Standard deviation of all laboratories and test samples for As (in general n = 6).**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 2.0$^{+}$ | 31$^{+}$ | 27$^{+}$ |
| 1 | 0.34 | 0.22 | 0.28 | 0.18 | 4.9 | 0.28 | 10 | 6.8 | 6.3 |
| 2 | | | | | | | | | |
| 3 | 0.14 | 0.11 | 0.16 | 0.27 | 2.7 | 0.20 | 3.8 | 2.5 | 15* |
| 4 | 0.73** | 0.69* | 0.69** | 1.3** | 11** | 0.35 | 6.7 | 11 | 11 |
| 5 | 0.31 | 0.12 | 0.30 | 0.82 | 4.8 | 0.14 | 15** | 10 | 4.4 |
| 6 | 0.04 | 0.05 | 0.13 | 0.18 | 1.9 | 0.19 | 2.8 | 2.6 | 2.8 |
| 7 | 0.11 | 0.27 | 0.15 | 1.3* | 2.4 | 0.16 | 3.8 | 3.9 | 5.1 |
| 8 | 0.31 | 0.43 | 0.38 | 0.56 | 5.2 | 0.54* | 12 | 15** | 15* |
| 9 | 0.12 | 0.19 | 0.14 | 0.43 | 6.7 | 0.15 | 9.6 | 1.7 | 4.3 |
| 10 | 0.084 | 0.69** | 0.13 | 0.15 | 1.5 | 0.14 | 2.7$^{x}$ | 2.0$^{x}$ | 2.0$^{x}$ |
| 11 | 0.45* | 0.92** | 0.52** | 1.0* | 7.3* | 0.62** | 44$^{+}$ | 20$^{+}$ | 45$^{+}$ |
| 12 | 0.25 | 0.10 | 0.29 | 0.16 | 2.8 | 0.022 | 1.0 | 1.2 | 2.8 |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 0.16 | 0.11 | 0.13 | | 1.9 | 0.081 | 2.5 | 4.5 | 7.3 |
| 15 | 0.82$^{-}$ | 0.28$^{-}$ | 0.14$^{-}$ | 0.48$^{-}$ | 3.5$^{-}$ | 0.37 | | | |
| 16 | 0.38 | 0.15 | 0.18 | 0.19 | 0.7 | 0.15 | 3.6 | 4.1 | 5.7 |

*$^{o}$: explosion in the digestion vessel, loss of samples*
*$^{+}$: Obvious irregularities (see annex 9)*
***: statistical outliers (see annex 9)*
**: stragglers(see annex 9)*
*$^{x}$: mistake on the dilution coefficient*
*$^{-}$: the reference values for $S_1$, $S_2$ and $S_3$ were known to NRL 15, values reported for information on the method of measurements (voltammetry).*
*$^{oo}$NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

**Table 19: Means of Cd for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 58.0 | 41.3 | 62.5 |
| 1 | 5.2 | 5.0 | 5.0 | 12.0 | 75.5 | 2.7 | 70.5$^{o}$ | 65.0$^{o}$ | 66.0$^{o}$ |
| 2 | | | | | | | | | |
| 3 | 6.7** | 6.7** | 7.3** | 15.0** | 85.9 | 3.0 | 93.3 | 95.3 | 103.9 |
| 4 | 5.1 | 4.9 | 4.8 | 11.6 | 70.1 | 3.4 | 90.6 | 88.7 | 87.1 |
| 5 | 4.8 | 5.0 | 5.0 | 11.0 | 71.2 | 3.7 | 113.0 | 113.3 | 119.7 |
| 6 | 5.1 | 5.2 | 5.2 | 10.1 | 71.1 | 3.6 | 108.4 | 103.7 | 108.8 |
| 7 | 5.0 | 5.2 | 4.7 | 11.1 | 49.1 | 2.1 | 70.7 | 70.0 | 62.0 |
| 8 | 5.3 | 5.2 | 5.3 | 11.8 | 73.5 | 3.2 | 100.2 | 97.0 | |
| 9 | 4.9 | 5.0 | 5.1 | 11.2 | 80.4 | 3.2 | 95.4 | 101.2 | 95.5 |
| 10 | 5.0 | 5.1 | 5.2 | 11.4 | 66.2 | 2.4 | 43.9$^{x}$ | 45.6$^{x}$ | 45.6$^{x}$ |
| 11 | 5.3 | 5.3 | 5.2 | 11.6 | 83.2 | 3.1 | 116.8 | 124.7 | 118.8 |
| 12 | 5.0 | 5.2 | 5.4 | 11.7 | 66.5 | 3.3 | 62.3$^{o}$ | 66.1$^{o}$ | 64.6$^{o}$ |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 5.1 | 5.1 | 5.1 | | 71.5 | 3.4 | 96.4 | 94.5 | 94.1 |
| 15 | 4.8$^{-}$ | 5.0$^{-}$ | 5.2$^{-}$ | 10.4$^{-}$ | 59.6$^{-}$ | 26.9$^{+}$ | 320.6$^{+}$ | 321.6$^{+}$ | 306.2+ |
| 16 | 4.6 | 6.3** | 5.1 | 9.4 | 60.0 | 2.7 | 72.1 | 86.1 | 86.2 |

**Table 20: Standard deviation of all laboratories and test samples for Cd (in general n = 6).**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 12** | 15** | 8.0** |
| 1 | 0.079 | 0.10 | 0.053 | 0.14 | 1.4 | 0.038 | 1.7 | 1.7 | 1.1 |
| 2 | | | | | | | | | |
| 3 | 0.067 | 0.10 | 0.10 | 0.082 | 0.79 | 0.10 | 0.5 | 2.3 | 9.1** |
| 4 | 0.33** | 0.22* | 0.29** | 0.34* | 3.9** | 0.17* | 4.3 | 3.3 | 4.4 |
| 5 | 0.068 | 0.035 | 0.065 | 0.090 | 1.1 | 0.043 | 3.0 | 2.5 | 3.7 |
| 6 | 0.10 | 0.056 | 0.044 | 0.21 | 1.4 | 0.13 | 1.0 | 3.3 | 1.7 |
| 7 | 0.10 | 0.17 | 0.13 | 0.22 | 0.70 | 0.022 | 1.8 | 1.4 | 1.2 |
| 8 | 0.25 | 0.083 | 0.064 | 0.10 | 0.45 | 0.14 | 3.8 | 3.0 | |
| 9 | 0.13 | 0.14 | 0.11 | 0.24 | 4.8** | 0.090 | 6.6** | 1.6 | 2.6 |
| 10 | 0.052 | 0.082 | 0.055 | 0.052 | 0.62 | 0.052 | 6.1** $^{x}$ | 5.5* | 5.5** $^{x}$ |
| 11 | 0.15 | 0.15 | 0.10 | 0.22 | 3.6** | 0.062 | 2.0 | 1.5 | 2.5 |
| 12 | 0.14 | 0.03 | 0.17 | 0.10 | 1.7 | 0.026 | 2.0 | 1.2 | 2.3 |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 0.046 | 0.049 | 0.056 | | 1.0 | 0.049 | 0.7 | 1.3 | 1.9 |
| 15 | 0.18$^{-}$ | 0.09$^{-}$ | 0.15$^{-}$ | 0.28$^{-}$ | 1.1$^{-}$ | 0.95 | 11$^{+}$ | 6.1$^{+}$ | 13$^{+}$ |
| 16 | 0.054 | 0.16 | 0.14 | 0.16 | 1.0 | 0.071 | 1.8 | 2.2 | 3.3 |

*$^{o}$: explosion in the digestion vessel, loss of samples*
*$^{+}$: Obvious irregularities (see annex 9)*
***: statistical outliers (see annex 9)*
**: stragglers (see annex 9)*
*$^{x}$: mistake on the dilution coefficient*
*$^{-}$: the reference values for $S_1$, $S_2$ and $S_3$ were known to NRL 15, values reported for information on the method of measurements (voltammetry).*
*$^{oo}$NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

**Table 21: Means of Ni for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 385 | 404 | 367 |
| 1 | 28.1 | 28.4 | 27.4 | 11.9 | 67.7 | 33 | 295$^{o}$ | 313$^{o}$ | 297$^{o}$ |
| 2 | | | | | | | | | |
| 3 | 28.0 | 27.6 | 28.1 | 13.0 | 75.1 | 34 | 447 | 438 | 454 |
| 4 | 27.7 | 26.7 | 26.4 | 13.2 | 80.3 | 34 | 448 | 454 | 423 |
| 5 | 30.4 | 31.1 | 30.7 | 13.6 | 70.9 | 39 | 540 | | |
| 6 | 32.0 | 30.4 | 29.1 | 14.1 | 95.1 | 41 | 643 | 635* | 697 |
| 7 | 23.0 | 25.6 | 22.0 | 10.6 | 52.0 | 31 | 344 | 361 | 306 |
| 8 | 27.0 | 26.8 | 27.5 | 11.3 | 72.6 | 25 | 417 | 411 | |
| 9 | 25.7 | 27.0 | 26.3 | 12.0 | 77.6 | 37 | 549 | 542 | 544 |
| 10 | 27.2 | 27.3 | 27.6 | 17.5 | 114.5 | 48 | 333$^{x}$ | 363$^{x}$ | 363$^{x}$ |
| 11 | 28.5 | 29.1 | 29.6 | 16.6 | 87.1 | 44 | 9522$^{+}$ | 10096$^{+}$ | 7955$^{+}$ |
| 12 | 26.3 | 28.9 | 30.6 | 13.1 | 74.2 | 42 | 315$^{o}$ | 275$^{o}$ | 331$^{o}$ |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 27.6 | 27.6 | 27.4 | | 75.6 | 29 | 445 | 440 | 438 |
| 15 | 27.7$^{-}$ | 28.6$^{-}$ | 27.9$^{-}$ | 10.4$^{-}$ | 77.4$^{-}$ | 29 | 532 | 503 | 525 |
| 16 | 27.5 | 30.3 | 28.3 | 10.9 | 82.8 | 39 | 643 | 819** | 608 |

**Table 22: Standard deviationd of all laboratories and test samples for Ni (in general n = 6).**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 25** | 23** | 13 |
| 1 | 0.41 | 0.38 | 0.33 | 0.08 | 0.56 | 2.2* | 7.8 | 4.0 | 5.4 |
| 2 | | | | | | | | | |
| 3 | 0.31 | 0.29 | 0.51 | 0.19 | 1.3 | 0.87 | 5.0 | 3.1 | 12 |
| 4 | 1.3* | 1.2 | 1.3* | 0.45 | 7.6$^{+}$ | 1.1 | 12 | 20 | 3.9 |
| 5 | 1.4** | 1.2* | 1.3* | 0.37 | 1.9 | 1.1 | 14 | | |
| 6 | 0.65 | 0.80 | 0.79 | 0.10 | 1.3 | 1.7 | 7.7 | 8.6 | 11 |
| 7 | 0.28 | 0.68 | 0.26 | 0.44 | 1.3 | 0.96 | 4.8 | 5.5 | 3.9 |
| 8 | 0.60 | 0.43 | 0.30 | 0.34 | 0.68 | 0.60 | 10 | 9.6 | |
| 9 | 0.55 | 0.62 | 0.36 | 0.19 | 3.6** | 0.67 | 46** | 14 | 8.3 |
| 10 | 0.16 | 0.17 | 0.35 | 0.29 | 1.4 | 0.84 | 4.9$^{x}$ | 7.4$^{x}$ | 7.4$^{x}$ |
| 11 | 0.56 | 1.16** | 0.78 | 0.33 | 2.0 | 2.3** | 558 | 1364 | 879 |
| 12 | 0.80 | 0.11 | 0.96* | 0.10 | 2.2 | 0.55 | 26 | 7.2 | 21 |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 0.33 | 0.16 | 0.32 | | 0.78 | 0.40 | 4.0 | 7.7 | 3.9 |
| 15 | 1.0$^{-}$ | 0.91$^{-}$ | 0.86$^{-}$ | 0.64$^{-}$ | 1.6$^{-}$ | 0.85 | 18 | 9.8 | 8.1 |
| 16 | 0.13 | 0.30 | 0.21 | 0.15 | 0.59 | 0.23 | 9.7 | 6.6 | 5.7 |

*$^{o}$: explosion in the digestion vessel, loss of samples*
*$^{+}$: Obvious irregularities (see annex 9)*
***: statistical outliers (see annex 9)*
**: stragglers (see annex 9)*
*$^{x}$: mistake on the dilution coefficient*
*$^{-}$: the reference values for $S_1$, $S_2$ and $S_3$ were known to NRL 15, values reported for information on the method of measurements (voltammetry).*
*$^{oo}$NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

**Table 23: Means of Pb for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 3550 | 3582 | 3563 |
| 1 | 54.9 | 53.3 | 55.8 | 988 | 6495 | 164 | 2692 ° | 2515 ° | 2562 ° |
| 2 | | | | | | | | | |
| 3 | 53.9 | 51.5 | 57.0 | 1008 | 6538 | 162 | 3743 | 3603 | 3852 |
| 4 | 47.7 | 47.6 | 46.2 | 964 | 6031 | 165 | 3729 | 3618 | 3630 |
| 5 | 52.7 | 52.6 | 49.7 | 1026 | 6406 | 179 | 4471 | 4631 | 4604 |
| 6 | 54.8 | 52.4 | 56.2 | 1203* | 6656 | 168 | 4209 | 4241 | 4388 |
| 7 | 46.3 | 48.2 | 41.8 | 922 | 4189** | 160 | 3148 | 3133 | 2785 |
| 8 | 52.4 | 55.1 | 53.6 | 1018 | 6294 | 182 | 3868 | 4018 | |
| 9 | 46.7 | 47.1 | 47.9 | 941 | 6503 | 164 | 4217 | 3728 | 3917 |
| 10 | 48.4 | 50.5 | 51.6 | 960 | 7063 | 170 | 2073$^{x}$ | 2106$^{x}$ | 2106$^{x}$ |
| 11 | 51.4 | 50.8 | 51.3 | 989 | 6311 | 205 | 7585$^{+}$ | 7609$^{+}$ | 7524$^{+}$ |
| 12 | 49.1 | 53.2 | 54.2 | 1100 | 6815 | 185 | 2046$^{o}$ | 2218$^{o}$ | 2191$^{o}$ |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 47.3 | 47.8 | 47.4 | | 6306 | 143 | 3642 | 3612 | 3630 |
| 15 | 48.6$^{-}$ | 50.1$^{-}$ | 50.1$^{-}$ | 1001$^{-}$ | 6675$^{-}$ | 172 | 3830 | 3891 | 3830 |
| 16 | 52.0 | 52.2 | 51.4 | 1029 | 6534 | 155 | 3935 | 3947 | 3931 |

**Table 24: Standard deviation of all laboratories and test samples for Pb (in general n = 6).**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 121* | 153** | 121 |
| 1 | 0.87 | 1.02 | 0.64 | 7.0 | 85 | 1.4 | 46 | 49 | 35 |
| 2 | | | | | | | | | |
| 3 | 0.55 | 0.59 | 1.09 | 5.7 | 33 | 1.9 | 40 | 29 | 148 |
| 4 | 1.99* | 0.87 | 1.04 | 12.4 | 103 | 3.6 | 57 | 67 | 37 |
| 5 | 1.25 | 1.09 | 1.10 | 22.1** | 55 | 2.1 | 107 | 81 | 92 |
| 6 | 0.72 | 0.70 | 0.87 | 12.1 | 49 | 1.0 | 55 | 45 | 163 |
| 7 | 0.98 | 1.13 | 1.27 | 11.6 | 47 | 0.8 | 24 | 33 | 30 |
| 8 | 1.42 | 1.04 | 1.64 | 7.3 | 20 | 2.5 | 42 | 56 | |
| 9 | 0.28 | 0.88 | 0.82 | 11.0 | 164 | 1.4 | 319** | 58 | 120 |
| 10 | 0.19 | 0.12 | 0.52 | 3.8 | 64 | 1.2 | 30$^{x}$ | 11$^{x}$ | 11$^{x}$ |
| 11 | 0.80 | 0.83 | 1.01 | 9.4 | 23 | 5.3 | 135 | 175 | 119 |
| 12 | 1.26 | 0.21 | 1.93* | 8.1 | 207** | 6.1** | 55 | 23 | 65 |
| 13 | | | | | | | | | |
| 14$^{oo}$ | 1.12 | 0.89 | 0.69 | | 134 | 2.1 | 23 | 49 | 47 |
| 15 | 1.33$^{-}$ | 0.85$^{-}$ | 1.21$^{-}$ | 35.0$^{-}$ | 173$^{-}$ | 3.9 | 67 | 78 | 157 |
| 16 | 0.49 | 0.41 | 0.42 | 5.9 | 31 | 0.7 | 21 | 35 | 27 |

*$^{o}$: explosion in the digestion vessel, loss of samples*
*$^{+}$: Obvious irregularities (see annex 9)*
***: statistical outliers (see annex 9)*
**: stragglers (see annex 9)*
*$^{x}$: mistake on the dilution coefficient*
*$^{-}$: the reference values for $S_1$, $S_2$ and $S_3$ were known to NRL 15, values reported for information on the method of measurements (voltammetry).*
*$^{oo}$NRL 14 analysed a cellulose ester filter PALL GN-4 Metricel while the other NRLs received a Whatman QMA quartz filter*

**Table 25: Means of Zn for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 12244* | 12236* | 12222* |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 70.8 | 72.2 | 67.2 | 756.3 | 4451 | 567.8 | 11434 | 11799 | 11567 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 87.0 | 83.6 | 80.8 | 764.6 | 3361 | | | | |
| 8 | 77.1 | 78.1 | 78.1 | 763.7 | 4938 | | | | |
| 9 | 69.0 | 70.4 | 70.2 | 687.1 | 4815 | | | | |
| 10 | 73.9 | 76.2 | 73.3 | 755.8 | 4801 | | | | |
| 11 | | | | | | | | | |
| 12 | 76.7 | 80.7 | 82.0 | 798.8 | 4637 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 76.6$^{-}$ | 83.6$^{-}$ | 87.2$^{-}$ | 757.2$^{-}$ | 4571 | 692 | 13025 | 14380 | 12484 |
| **16** | 64.7 | 132.5 | 61.1 | 642.0 | 3844 | 436.7 | 9171 | 10282 | 9471 |

**Table 26: Standard deviation of all laboratories and test samples for Zn (in general n = 6)**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 118 | 64 | 81 |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 3.7 | 1.7 | 4.0 | 7.7 | 93 | 13 | 114 | 384 | 155 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 1.7 | 2.2 | 1.7 | 28 | 32 | | | | |
| 8 | 0.74 | 0.67 | 0.40 | 4.3 | 38 | | | | |
| 9 | 0.78 | 1.0 | 1.1 | 4.8 | 104 | | | | |
| 10 | 0.36 | 1.8 | 1.0 | 7.0 | 82 | | | | |
| 11 | | | | | | | | | |
| 12 | 2.0 | 0.67 | 2.8 | 14 | 331 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 5.1$^{-}$ | 3.6 | 4.0$^{-}$ | 85$^{-}$ | 281$^{-}$ | 52 | 1566 | 1749 | 1138 |
| **16** | 0.65 | 1.3 | 0.40 | 2.8 | 17 | 4.4 | 66 | 55 | 32 |

*$^{-}$: the reference values for $S_1$, $S_2$ and $S_3$ were known to NRL 15, values reported for information on the method of measurements (voltammetry).*
**: values reported by NRL 0 after distribution of the results of the IE.*

**Table 27: Means of Cu for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 5765* | 5772* | 5827* |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 28.14 | 27.91 | 26.64 | 93.0 | 598 | 536 | 6314 | 6223 | 6148 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 25.00 | 26.83 | 23.78 | 76.9 | 377.8 | | | | |
| 8 | 28.75 | 28.58 | 28.98 | 92.3 | 584 | | | | |
| 9 | 26.69 | 27.32 | 27.25 | 87.0 | 570 | | | | |
| 10 | 26.80 | 27.10 | 27.47 | 87.4 | 537 | | | | |
| 11 | | | | | | | | | |
| 12 | 28.05 | 30.34 | 31.32 | 95.1 | 569 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 29.46$^{-}$ | 30.09$^{-}$ | 30.37$^{-}$ | 91.4$^{-}$ | 591$^{-}$ | 519 | 6037 | 5900 | 5865 |
| **16** | 25.42 | 29.51 | 25.79 | 84.0 | 488.5 | 407 | 5992 | 6154 | 6042 |

**Table 28: Standard deviation of all laboratories and test samples for Cu (in general n = 6)**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 58 | 60 | 72 |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 1.24 | 1.00 | 0.81 | 2.9 | 19 | 13 | 96 | 149 | 97 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 0.42 | 0.77 | 0.60 | 3.2 | 4.1 | | | | |
| 8 | 0.23 | 0.39 | 0.21 | 0.86 | 4.2 | | | | |
| 9 | 0.26 | 0.44 | 0.41 | 0.73 | 9.5 | | | | |
| 10 | 0.179 | 0.24 | 0.34 | 0.95 | 4.0 | | | | |
| 11 | | | | | | | | | |
| 12 | 0.79 | 0.11 | 1.10 | 0.54 | 13.0 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | 0.90$^{-}$ | 0.53$^{-}$ | 0.62$^{-}$ | 4.30$^{-}$ | 22.1$^{-}$ | 9.1 | 121 | 278 | 156 |
| **16** | 0.17 | 0.29 | 0.15 | 0.35 | 3.4 | 1.8 | 26 | 37 | 22 |

*$^{-}$: the reference values for $S_1$, $S_2$ and $S_3$ were known to NRL 15, values reported for information on the method of measurements (voltammetry).*
**: values reported by NRL 0 after distribution of the results of the IE.*

**Table 29: Means of Cr for all laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 822* | 792 | 792* |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 27.88 | 28.66 | 27.38 | 51.3 | 149 | 72.5 | 844 | 825 | 805 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 25.93 | 24.63 | 23.98 | 38.7 | 77.6 | | | | |
| 8 | 28.87 | 29.16 | 29.91 | 49.7 | 408 | | | | |
| 9 | 26.57 | 27.14 | 26.62 | 47.3 | 104 | 28.4* | 881* | 846* | 842* |
| 10 | 25.78 | 26.43 | 26.68 | 44.8 | 119 | | | | |
| 11 | | | | | | | | | |
| 12 | 26.71 | 29.32 | 30.50 | 50.3 | 97 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 28.36 | 32.85 | 28.61 | 42.1 | 147.4 | 68.4 | 980 | 1620 | 957 |

**Table 30: Standard deviation of all laboratories and test samples for Cr (in general n = 6).**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 19 | 49 | 54 |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 2.13 | 2.06 | 2.23 | 2.0 | 14 | 2.7 | 33 | 46 | 47 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 0.52 | 0.82 | 0.41 | 2.0 | 1.2 | | | | |
| 8 | 0.35 | 0.40 | 0.26 | 0.50 | 1.7 | | | | |
| 9 | 0.16 | 0.75 | 0.31 | 0.87 | 4.1 | 1.0 | 68 | 30 | 33 |
| 10 | 0.28 | 0.26 | 0.28 | 0.46 | 3.1 | | | | |
| 11 | | | | | | | | | |
| 12 | 0.90 | 0.33 | 1.37 | 0.35 | 3.8 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 0.21 | 0.38 | 0.19 | 0.51 | 1.4 | 0.61 | 14 | 33 | 9.6 |

**: values reported by NRL 0 and 9 after distribution of the results of the IE.*

**Table 31: Means of Mn for all the laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 1669* | 1702* | 1685* |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 70.3 | 70.6 | 68.0 | 127 | 743 | 143 | 1831 | 1827 | 1792 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 61.4 | 69.1 | 60.2 | 106 | 524 | | | | |
| 8 | 75.3 | 76.4 | 77.3 | 128 | 823 | | | | |
| 9 | 66.0 | 66.8 | 65.5 | 114 | | 119* | 1835* | 1823* | 1752* |
| 10 | 67.9 | 67.0 | 73.1 | 120 | 686 | | | | |
| 11 | | | | | | | | | |
| 12 | 68.8 | 75.3 | 77.9 | 128 | 753 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 72.2 | 70.3 | 70.5 | 121 | 730 | 128 | 1868 | 1840 | 1826 |

**: values reported by NRL 0 and 9 after distribution of the results of the IE.*

**Table 32: Standard deviation of all laboratories and test samples for Mn**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | 61 | 27 | 40 |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 2.65 | 1.41 | 1.15 | 1.8 | 9 | 2.1 | 26 | 47 | 20 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 1.24 | 2.12 | 1.69 | 4.2 | 6 | | | | |
| 8 | 0.36 | 0.18 | 0.21 | 0.5 | 3 | | | | |
| 9 | 0.75 | 1.22 | 0.75 | 1.7 | | 3.1 | 119 | 21 | 46 |
| 10 | 0.36 | 0.51 | 0.90 | 1.0 | 10 | | | | |
| 11 | | | | | | | | | |
| 12 | 1.87 | 0.46 | 2.68 | 1.3 | 21 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 0.47 | 0.61 | 0.54 | 0.4 | 1 | 0.3 | 12 | 16 | 11 |

**Table 33: Means of Co for all the laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | | | |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 9.61 | 9.69 | 9.13 | | | 2.8 | 33 | 32 | 30 |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | 9.16 | 9.14 | 8.74 | | | | | | |
| 8 | | | | | | | | | |
| 9 | 9.36 | 9.53 | 9.41 | | | | | | |
| 10 | 9.08 | 9.15 | 9.30 | | | | | | |
| 11 | | | | | | | | | |
| 12 | 9.66 | 10.06 | 10.38 | | | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 9.82 | 10.58 | 9.88 | 2.3 | 15.1 | 2.9 | 29.2 | 41.4 | 37 |

**Table 34: Means of V for all the laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | | | |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | 28.0 | 28.3 | 26.9 | 20.8 | 112.3 | 14 | 225 | 223 | 216 |
| 5 | | | | | | | | | |
| 6 | 23.6 | 24.5 | 23.8 | 19.7 | 107.8 | | | | |
| 7 | 25.1 | 24.8 | 23.3 | 15.6 | 77.9 | | | | |
| 8 | 27.2 | 27.8 | 28.4 | 19.4 | 127.2 | | | | |
| 9 | | | | | | | | | |
| 10 | 24.8 | 25.1 | 25.6 | 17.8 | 90.1 | | | | |
| 11 | | | | | | | | | |
| 12 | 27.1 | 29.4 | 30.3 | 20.7 | 105.3 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 27.5 | 30.0 | 27.4 | 16.3 | 104.1 | 11 | 198 | 221 | 216 |

**Table 35: Means of Fe for all the laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | | | |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | | | | 4919 | 26225 | | | | |
| 8 | | | | 6191 | 38804 | | | | |
| 9 | | | | | | | | | |
| 10 | | | | 5136 | 25563 | | | | |
| 11 | | | | | | | | | |
| 12 | | | | 6553 | 33761 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| **16** | 933.3 | 859.7 | 880.3 | 5821 | 34060 | 9455 | 125727 | 123467 | 119728 |

**Table 36: Means of Al for all the laboratories and test samples.**

| Samples | S1 | S1 | S1 | S2 | S3 | S4 | S5 | S5 | S5 |
|---|---|---|---|---|---|---|---|---|---|
| Lab. | ng/ml | ng/ml | ng/ml | ng/ml | mg/kg | ng/ml | ng | ng | ng |
| 0 | | | | | | | | | |
| 1 | | | | | | | | | |
| 2 | | | | | | | | | |
| 3 | | | | | | | | | |
| 4 | | | | | | | | | |
| 5 | | | | | | | | | |
| 6 | | | | | | | | | |
| 7 | | | | 3472 | 13240 | | | | |
| 8 | | | | 5103 | 34161 | | | | |
| 9 | | | | 50.9* | | | | | |
| 10 | | | | 4180 | 8407 | | | | |
| 11 | | | | | | | | | |
| 12 | | | | 6266 | 16477 | | | | |
| 13 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| 16 | 1170 | 1133 | 1130 | 5409 | 19864 | 1480 | 18344 | 17723 | 17282 |

*Lab. 9 informed, after the results were published that they made a mistake using their dilution factor, their results should have been 5090 ng/ml*

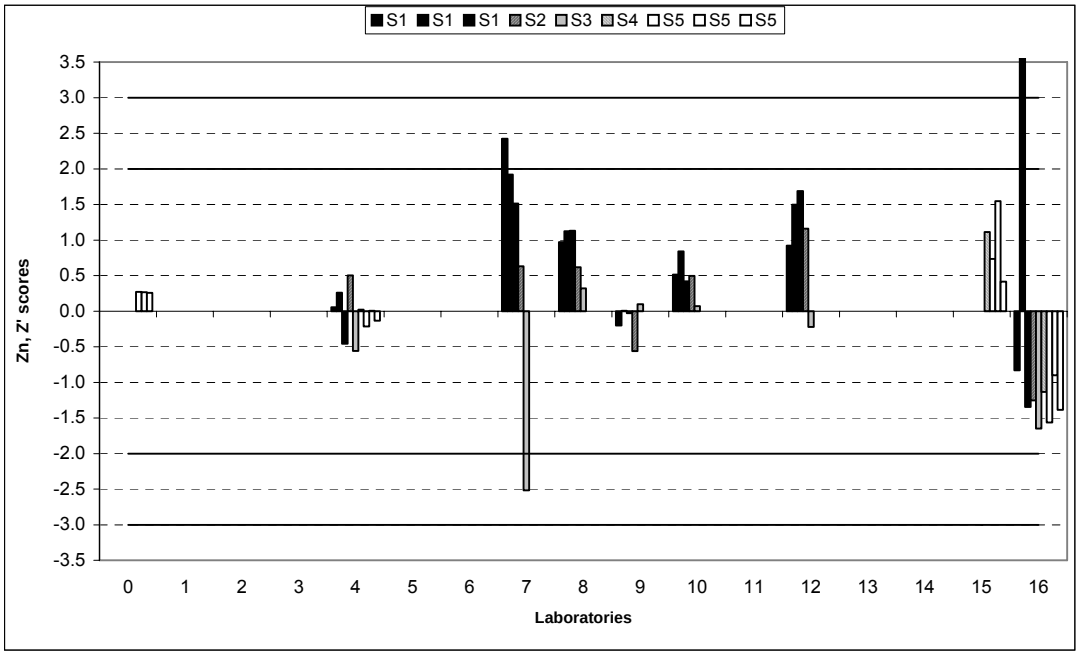



**Figure 21: z' score for Zn**

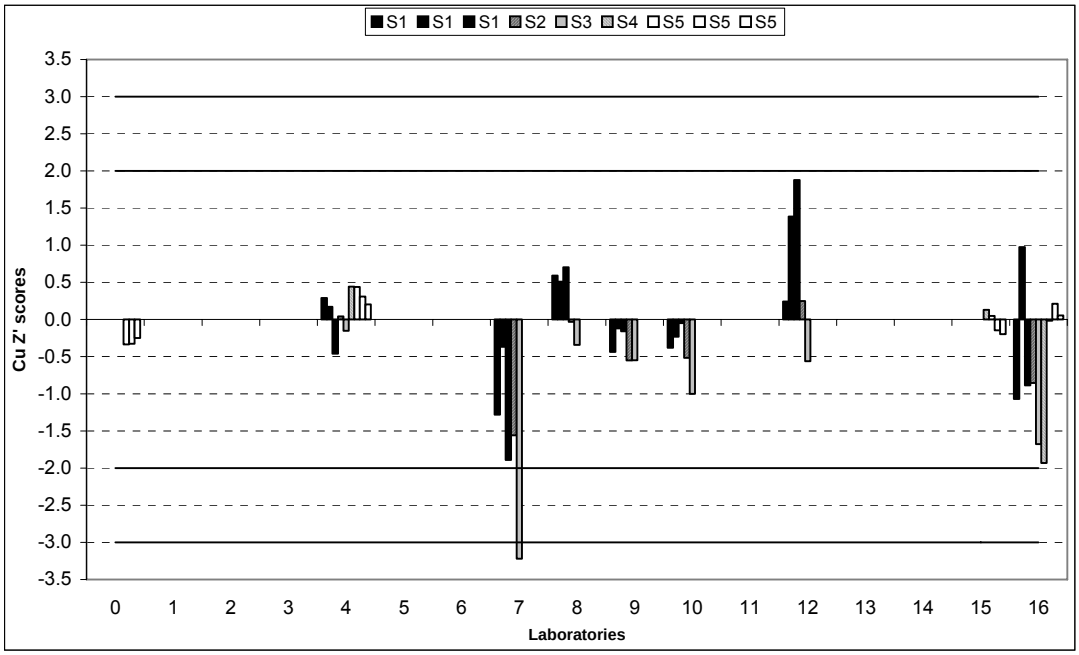



**Figure 22: z'score for Cu**

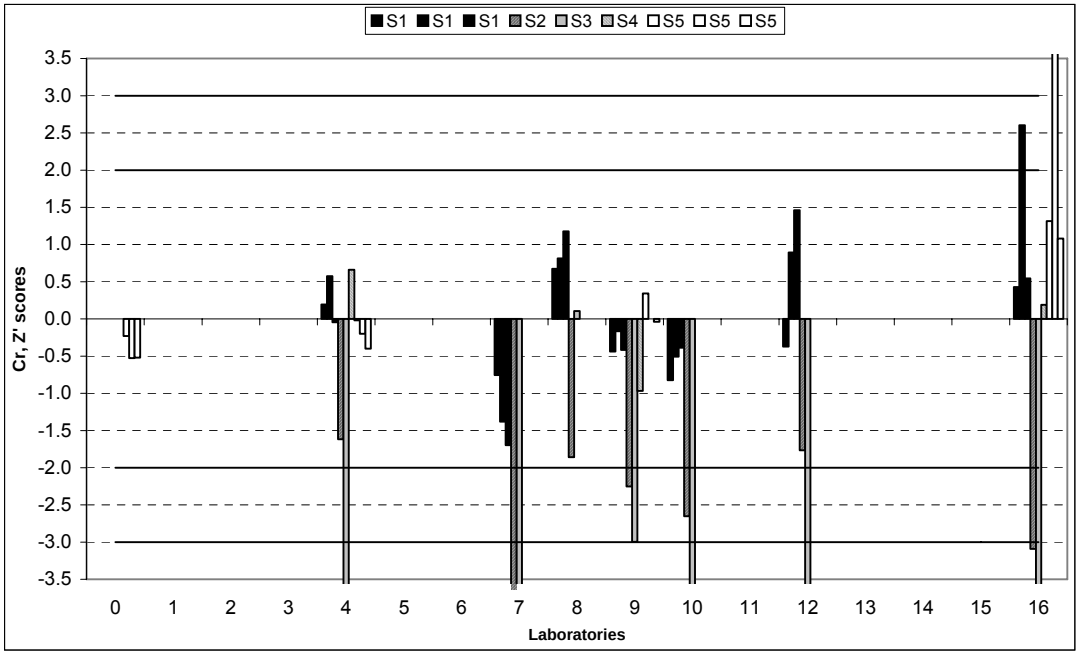



**Figure 23: z'score for Cr**

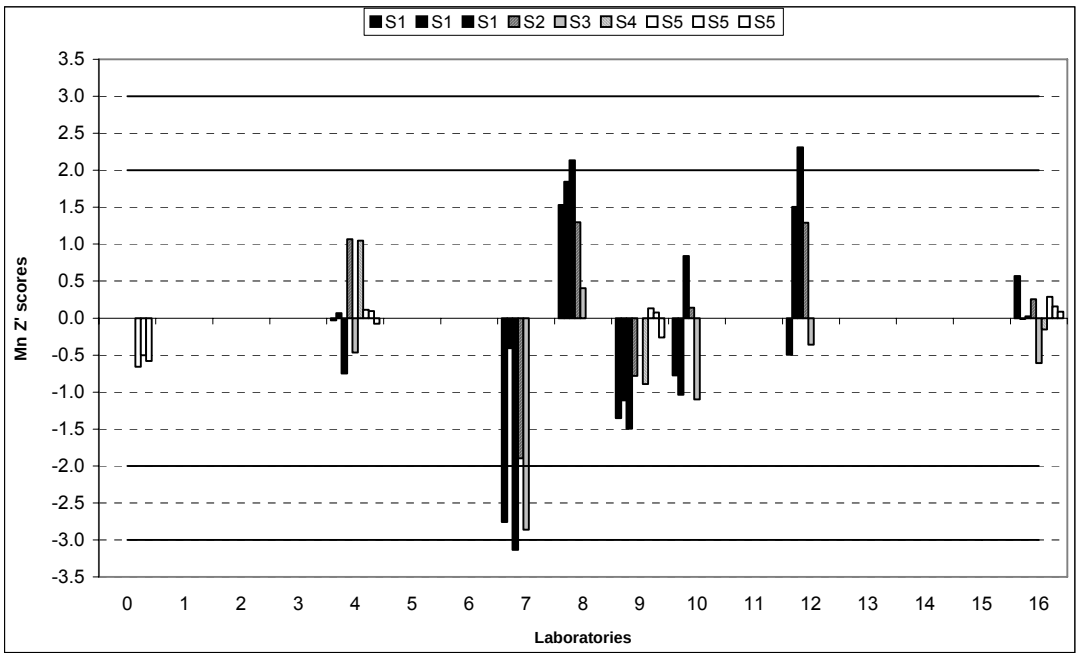



**Figure 24: z'score for Mn**

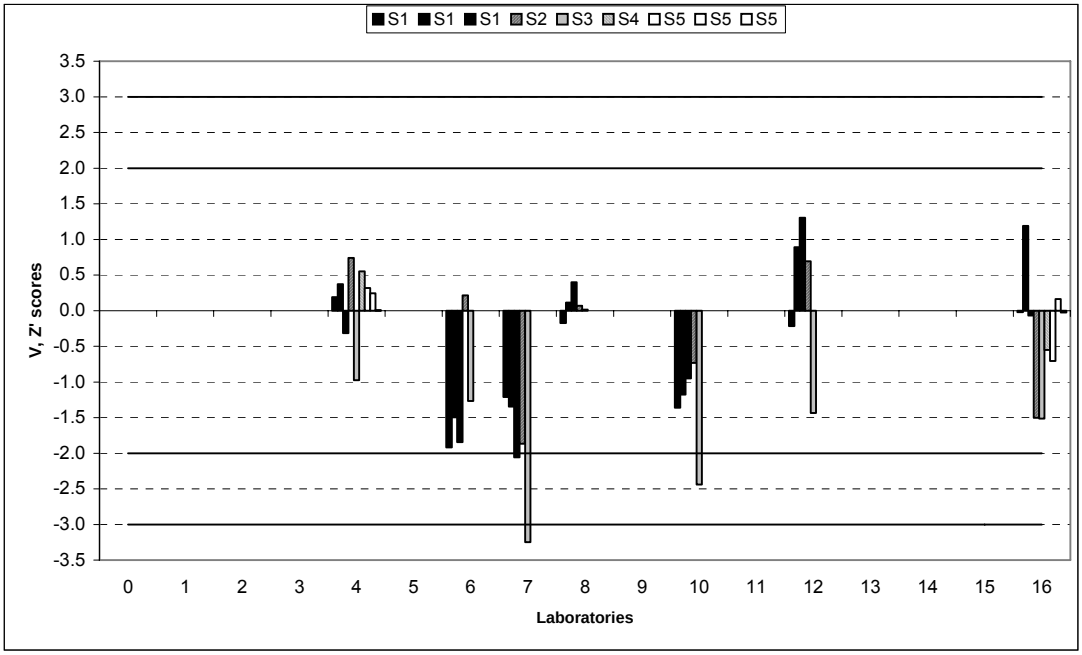



**Figure 25: z'score for V**

**Table 37 Reagent blank ($S_1$ in ng/ml) and filter blank ($S_5$ in ng) values for all participants**

| | As | | | | Cd | | | | Ni | | | | Pb | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | S1 | | S5 | | S1 | | S5 | | S1 | | S5 | | S1 | | S5 | |
| | Mean | s | Mean | s | Mean | s | Mean | s | Mean | s | Mean | s | Mean | s | Mean | s |
| Lab. 0 | | | | 7.09 | | | | 14.87 | | | | 17.59 | | | | 81.06 |
| Lab. 1 | | 0.12 | | 0.07 | | 0.14 | | 0.02 | | 0.13 | | 0.30 | | 0.22 | | 0.16 |
| Lab. 2 | | | | | | | | | | | | | | | | |
| Lab. 3 | 0.03 | 0.01 | 3.86 | 2.63 | 0.00 | 0.00 | 0.39 | 0.17 | 0.12 | 0.04 | 42.10 | 2.70 | 0.19 | 0.10 | 24.30 | 3.41 |
| Lab. 4 | -1.31 | 1.51 | 1.85 | 1.69 | -0.03 | 0.60 | 1.74 | 0.67 | -0.52 | 1.86 | 30.20 | 5.22 | 0.42 | 0.62 | 7.86 | 1.87 |
| Lab. 5 | 0.4 | 1.2 | 5.1 | 1.3 | 0.3 | 0.2 | 46 | 6 | 13 | 9.4 | 76 | 5 | 16 | 7.8 | 145 | 24.8 |
| Lab. 6 | 0.41 | 0.15 | 23.25 | 8.10 | 0.00 | 0.00 | 0.55 | 0.06 | -0.35 | 0.07 | 34.30 | 5.00 | 0.03 | 0.03 | 25.01 | 8.00 |
| Lab. 7 | 0.53 | 0.93 | 1.01 | 1.28 | 1.44 | 1.86 | 5.66 | 0.28 | 2.41 | 0.56 | 21.84 | 1.51 | 3.23 | 0.35 | 6.84 | 0.21 |
| Lab. 8 | -0.01 | 0.01 | -2.60 | 16.34 | 0.00 | 0.00 | 2.13 | 3.68 | 0.02 | 0.05 | 251.99 | 8.34 | 0.07 | 0.04 | 140.73 | 37.46 |
| Lab. 9 | | < 0.5 | | < 25 | | < 0.1 | | < 5 | | < 1 | | < 50 | | 1.60 | | 55.00 |
| Lab. 10 | 0.00 | 0.00 | 2.22 | 0.05 | -0.07 | 0.01 | -5.56 | 0.10 | -0.03 | 0.00 | 8.06 | 0.18 | 0.74 | 0.43 | 48.06 | 0.07 |
| Lab. 11 | | 0.82 | | 14.40 | | 0.15 | | 7.30 | | 0.81 | | 7417** | | 10.80 | | 456.00 |
| Lab. 12 | 0.45 | 0.15 | < 0,6 | 0 | < 0,1 | 0 | 0.05 | 0.4 | 31.00 | 3 | 13.00 | 63.00 | 3.60 | 0.2 | 0.40 | 16.00 |
| Lab. 13 | | | | | | | | | | | | | | | | |
| Lab. 14* | 0.14 | 0.03 | <10 | 2.98 | 0.02 | 0.00 | <2.5 | 0.15 | 0.19 | 0.00 | 67.99 | 1.17 | 0.26 | 0.04 | 19.27 | 1.79 |
| Lab. 15 | 5.23 | 7.00 | 8.39 | 2.11 | 9.13 | 7.00 | 1.15 | 0.56 | 35.75 | 7.00 | 73.54 | 7.16 | 61.18 | 7.00 | 47.28 | 7.18 |
| Lab. 16 | | 0.01 | | 0 | | 0.00 | | 0.00 | | 0.00 | | 0.71 | | 0.04 | | 0.56 |

**: NRL 14 analysed a Pall filter cellulose esters while the other NRLs analysed a Whatman QMA quartz filter*

***: contamination*

# Annex 9: Scrutiny of results for consistency and statistical outliers

Hereafter the procedure developed in ISO 5725-2 to discard outliers from the determination of repeatability/reproducibility of a method is applied. First the Mandel k and h statistics were plotted to have an idea of the potential outliers (see Figure 26 - Figure 33). Then the full set of numerical outlier tests were applied: Cochran's test (outliers where discarded only if Grubbs' test for maximum or minimum within cell was significant) then Grubbs' test for mean (for one or two outliers on the means for maximum or minimum value). Where outliers were detected, they were discarded and the statistical test was then repeated until no more outliers could be detected

NRL 1 and 12 had an explosion in the oven when digesting filter $S_5$ with evaporation and loss of liquid, therefore their results were discarded. NRL 10 made a mistake on the coefficient of dilution thus its results were discarded.

## Arsenic

Obvious irregularities: For $S_5$, NRL 0 using EDXRF, reported 2, 3 and 2 values per set. These were near the laboratory limit of detection (25 ng) with relative standard deviation up to 60 %. It was decided to discard all the results of NRL 0. For $S_5$, NRL 11 reported values and standard deviation 3 to 4 times bigger than the other NRLs. The values of NRL 11 for $S_5$ were discarded.

NRL 4 produced a set of statistical outliers and stragglers for $S_1$, $S_2$, and $S_3$ when applying the Cochran's test without significant maximum or minimum in each cell. All values were discarded.

NRL 11 produced a set of statistical outliers and stragglers for $S_1$, $S_2$, $S_3$ and $S_4$ when applying the Cochran's test without significant maximum or minimum in each cell. All values were discarded.

NRL 5, the 1st set of $S_5$ was a statistical outlier when applying the Cochran's test. However, no high or low value in the cell was evidenced. No value was discarded.

NRL 7, $S_2$ was a straggler when applying the Cochran's test. However, as no high or low value in the cell was evidenced no value was discarded.

NRL 8 had a statistical outlier on $S_4$ applying the Grubb's'test for average. The same set was also a straggler for the Cochran's test. All the results for $S_4$ were discarded. The 2nd set of $S_5$ was a statistical outlier when applying the Cochran's test. However, as no high or low value in the cell was evidenced, no value was discarded.

NRL 10, the 2nd set of $S_1$ was a statistical outlier when applying the Cochran's test. However, as no high or low value in the cell was evidenced, no value was discarded.

The 3rd set of $S_1$ of NRL 3 and of NRL 10 were stragglers when applying the Grubbs' test for 2 maximum. They were retained.

## Cadmium

One obvious irregularity was observed for NRL 15, the analysis of $S_4$ and $S_5$ were discarded, likely due to an interference with Thallium.

NRL 0: For $S_5$, the 1st and 2nd sets were strong outliers when applying the Cochran's test while the 2nd one was a straggler, all $S_5$ results were discarded.

NRL 3: The 3rd set of $S_5$ was an outlier applying the Cochran's test. However, as no high or low value in the cell was evidenced, no value was discarded. For $S_1$, the 1st and 3rd sets were outliers while the 2nd one was a straggler when applying the Grubbs' test on the mean, therefore all $S_1$ results were discarded. Sample $S_2$ was also an outlier when applying the Grubbs' test on the mean and was discarded.

NRL 4 produced a set of outliers and stragglers for $S_1$, $S_2$, $S_3$ and $S_4$, when applying the Cochran's test. All values were discarded.

NRL 9: for $S_3$, one determination (70.9 mg/kg) in the set of 6 analysis was an outlier when applying Cochran's test (C = 0.366) and was discarded. It was confirmed by the Grubbs' test on minimum value of a cell. The 1st set of $S_5$ was a statistical outlier when applying the Cochran's test. However, as no high or low value in the cell was evidenced no value was discarded.

NRL 11: for $S_3$, one determination (89.7 mg/kg) in the set of 6 analysis was an outlier values when applying Cochran's test (C = 0.314) and was discarded.

NRL 16: the 2nd set of $S_1$ was an outlier when applying the Grubbs' test and was discarded.

## Nickel

One obvious irregularities was observed for the analysis of $S_5$ by NRL 11 with values 20 times higher than any other laboratory. Sample $S_3$ of NRL 4 had 4 times higher standard deviation than other NRLs. All these values were discarded

NRL 4: the 1st and 3rd sets of $S_1$ were stragglers when applying the Cochran's test. Sample $S_3$ was a statistical outlier when applying the Cochran's test. No high or low value in the cell was evidenced so that no value was discarded. However NRL 4 gave higher variability from sample S1 to S3 and it was decided to discard all its results.

NRL 5, the 1st, 2nd and 3rd set of $S_1$ were statistical outlier or straggler when applying the Cochran's test. Even though no high or low value were evidenced using the Grubbs' test, all value were discarded as NRL 5 gave higher variability than other participants.

NRL 12, the 3rd set of $S_1$ was a straggler when applying the Cochran's test. However, as no high or low value in the cell was evidenced no value was discarded.

NRL 11, the 2nd set of $S_1$ and sample $S_4$ were statistical outliers when applying the Cochran's test. However, as no high or low value in the cell was evidenced no value was discarded.

NRL 9, Sample $S_3$ was a statistical outlier when applying the Cochran's test and Grubbs' test for low values in a cell. The outlier was caused by 1 low value (70.3) which was cancelled. The 1st set of S5 was a statistical outlier when applying the Cochran's test. It was cause by two high values which were cancelled.

NRL 1, $S_4$ was a straggler when applying the Cochran's test and for the Grubbs' test for high values in a cell. The outlier was caused by 1 high value (37.1) which was cancelled.

NRL 0, the 1st and 2nd set of $S_5$ were a statistical outliers when applying the Cochran's test. However, as no high or low value in the cell was evidenced no value was discarded.

NRL 16, the 2nd set of $S_5$ was a straggler when applying the Grubbs' test for average in a cell. Two statistical outliers weres evidenced when applying the Grubbs' test for 2 highest means. Its results were discarded.

NRL 6, the 2nd set of $S_5$ was a straggler when applying the Grubbs' test for averages. Its results were not discarded.

## Lead

One obvious irregularities on $S_5$ for the analysis of Pb by NRL 11 with values 3000 ng higher than any other laboratory. All the values were discarded.

NRL 4, the 1st set of $S_1$ were stragglers when applying the Cochran's test. As no high or low value in the cell was evidenced no value was discarded.

NRL 12, the 3rd set of $S_1$ was a straggler when applying the Cochran's test. Samples $S_3$ and $S_4$ were found statistical outliers when applying the Cochran's test. However, as no high or low value were evidenced no value was discarded.

NRL 5, sample $S_2$ was found a statistical outlier when applying the Cochran's test. However, as no high or low value were evidenced no value was discarded.

NRL 9, the 1st set of $S_5$ was a statistical outlier when applying the Cochran's test and Grubbs' test for high values in a cell. The outlier was caused by 2 high values which were cancelled.

NRL 0, the 1st and 2nd sets of sample $S_5$ were stragglers and statistical outliers when applying the Cochran's test. However, as no high or low value were evidenced no value was discarded.

NRL 6, sample $S_2$ was a straggler when applying the Grubbs' test for average of cells. The value was not discarded.

NRL 7, sample $S_3$ was a statistical outlier when applying the Grubbs' test for average of cells. The value was discarded.

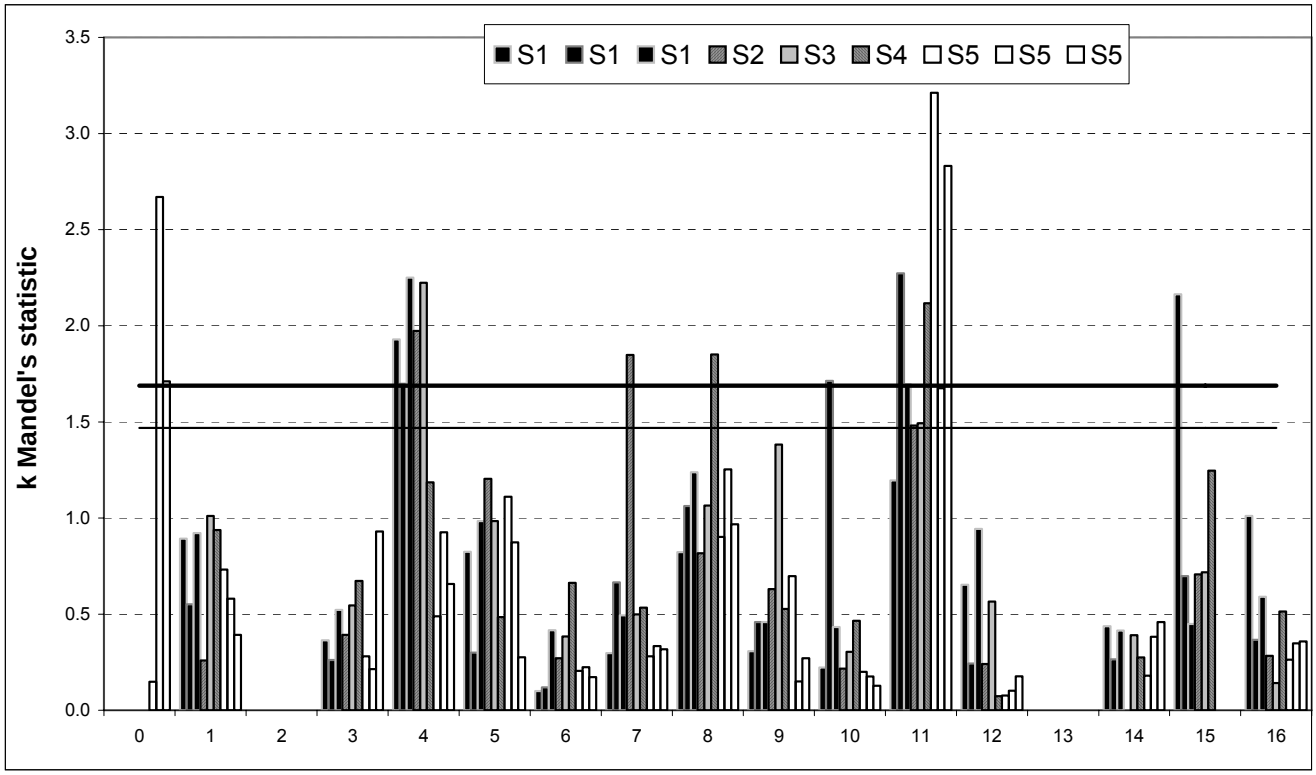



**Figure 26:** Mandel's k statistic for As versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's k statistic before any obvious irregularities and statistical outliers were cancelled.

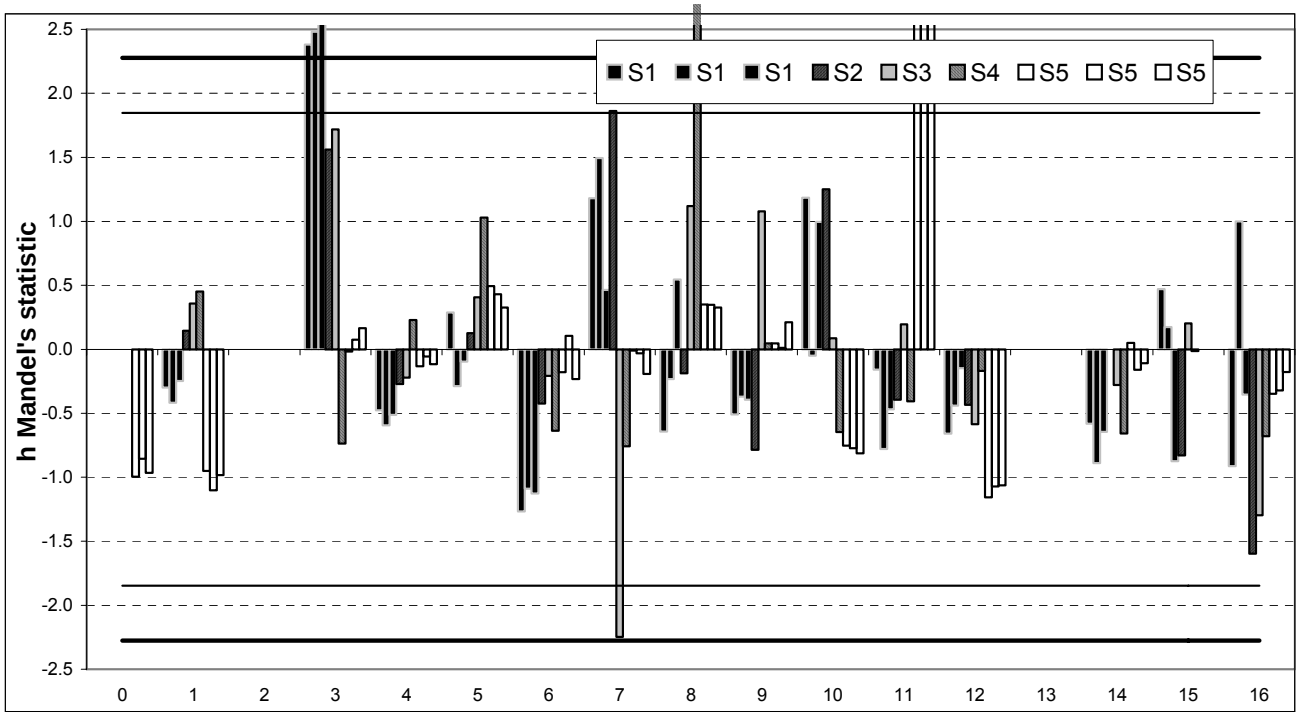



**Figure 27:** Mandel's h statistic for As versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's h statistic before any obvious irregularities and statistical outliers were cancelled.

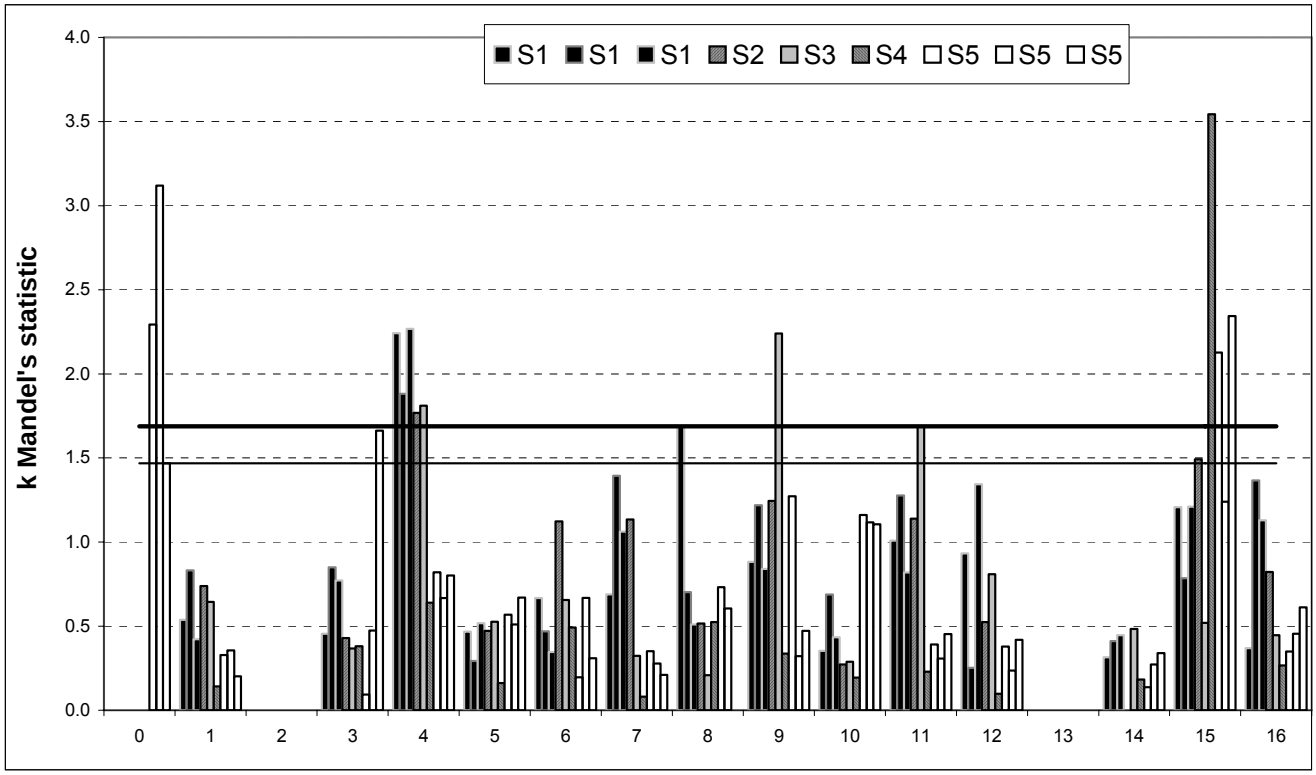



**Figure 28:** Mandel's k statistic for Cd versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's k statistic before any obvious irregularities and statistical outliers were cancelled.

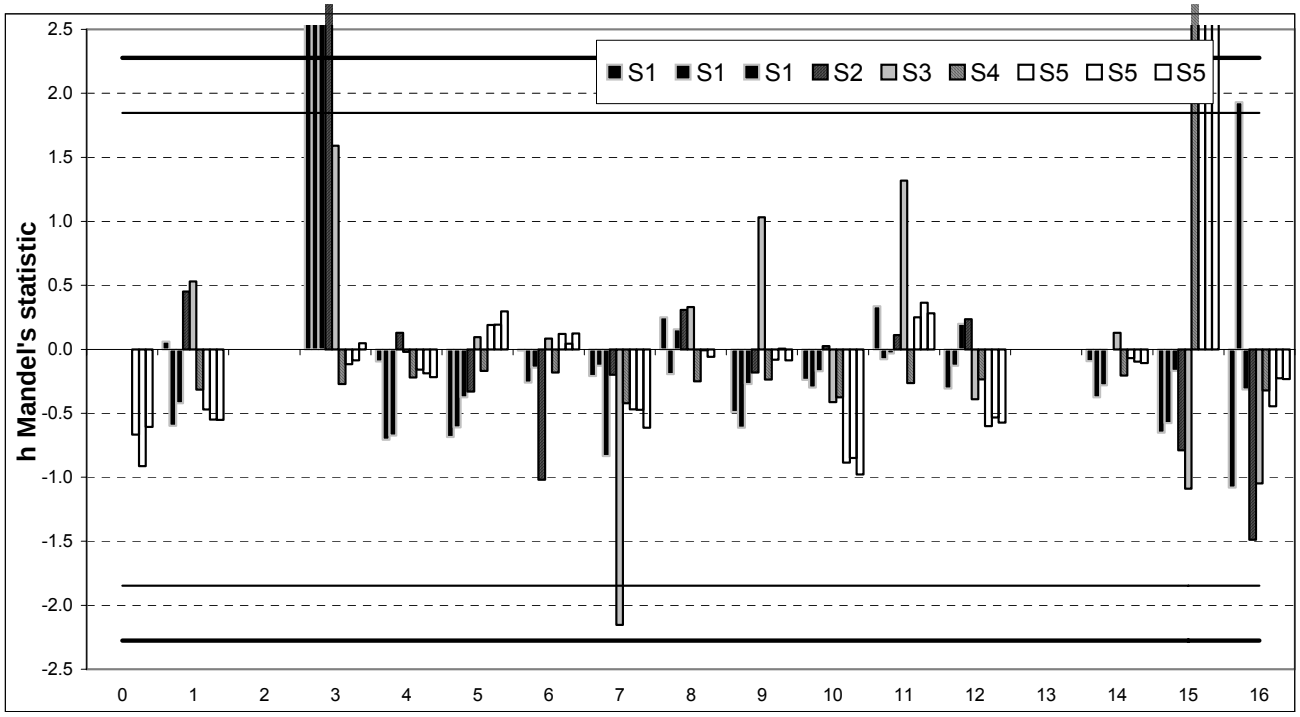



**Figure 29:** Mandel's h statistic for Cd versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's h statistic before any obvious irregularities and statistical outliers were cancelled.

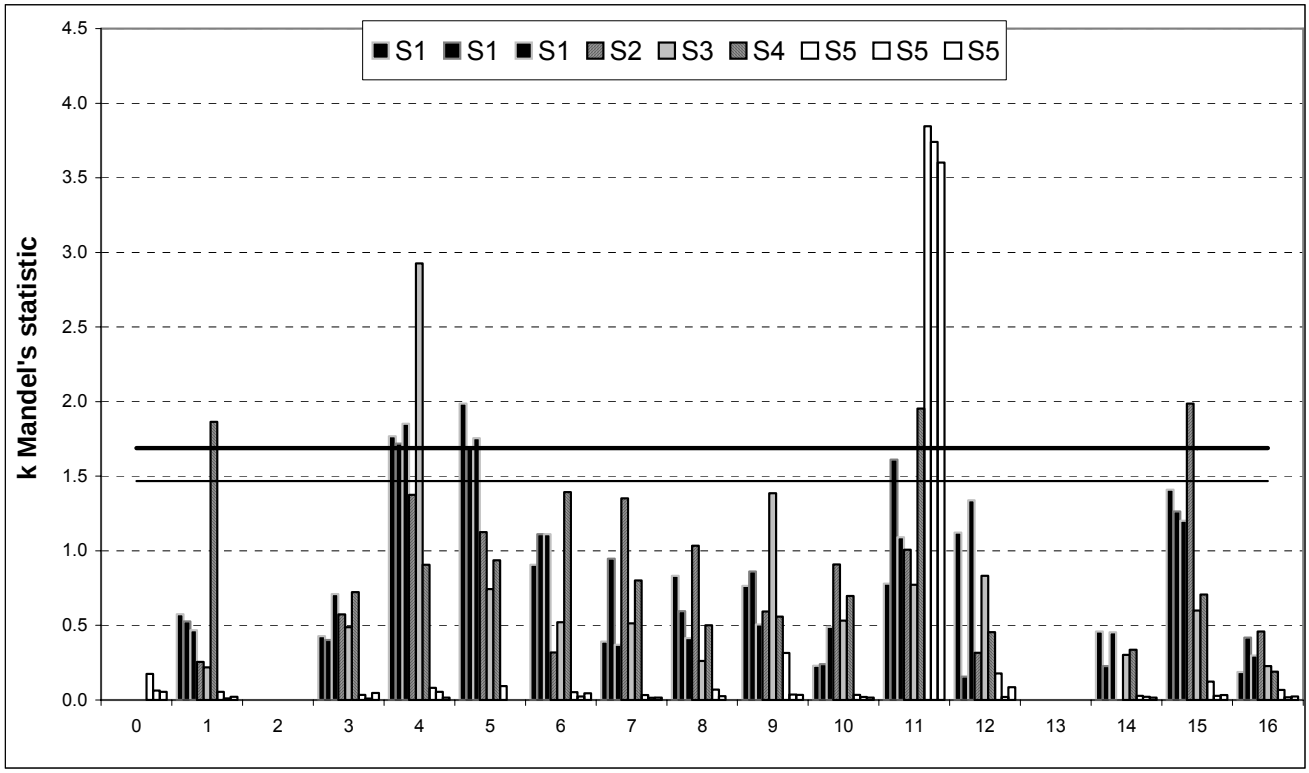



**Figure 30:** Mandel's k statistic for Ni versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's k statistic before any obvious irregularities and statistical outliers were cancelled.

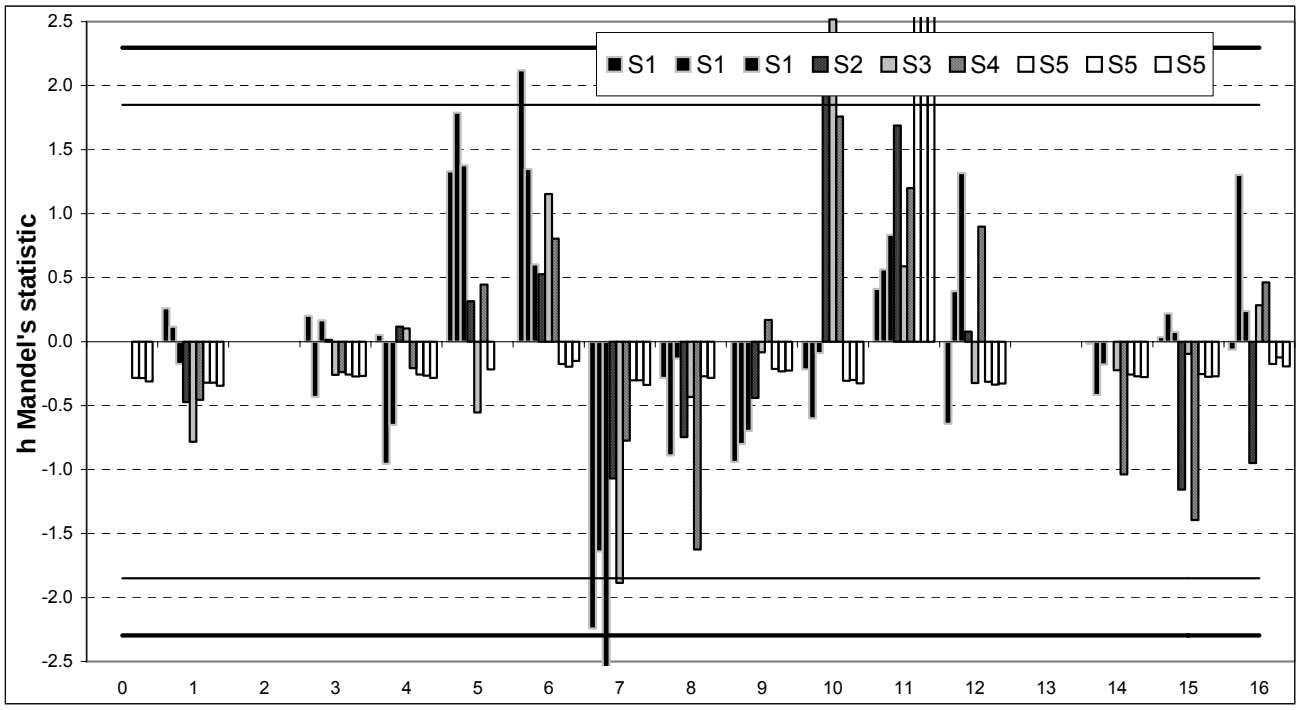



**Figure 31:** Mandel's h statistic for Ni versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's h statistic before any obvious irregularities and statistical outliers were cancelled.

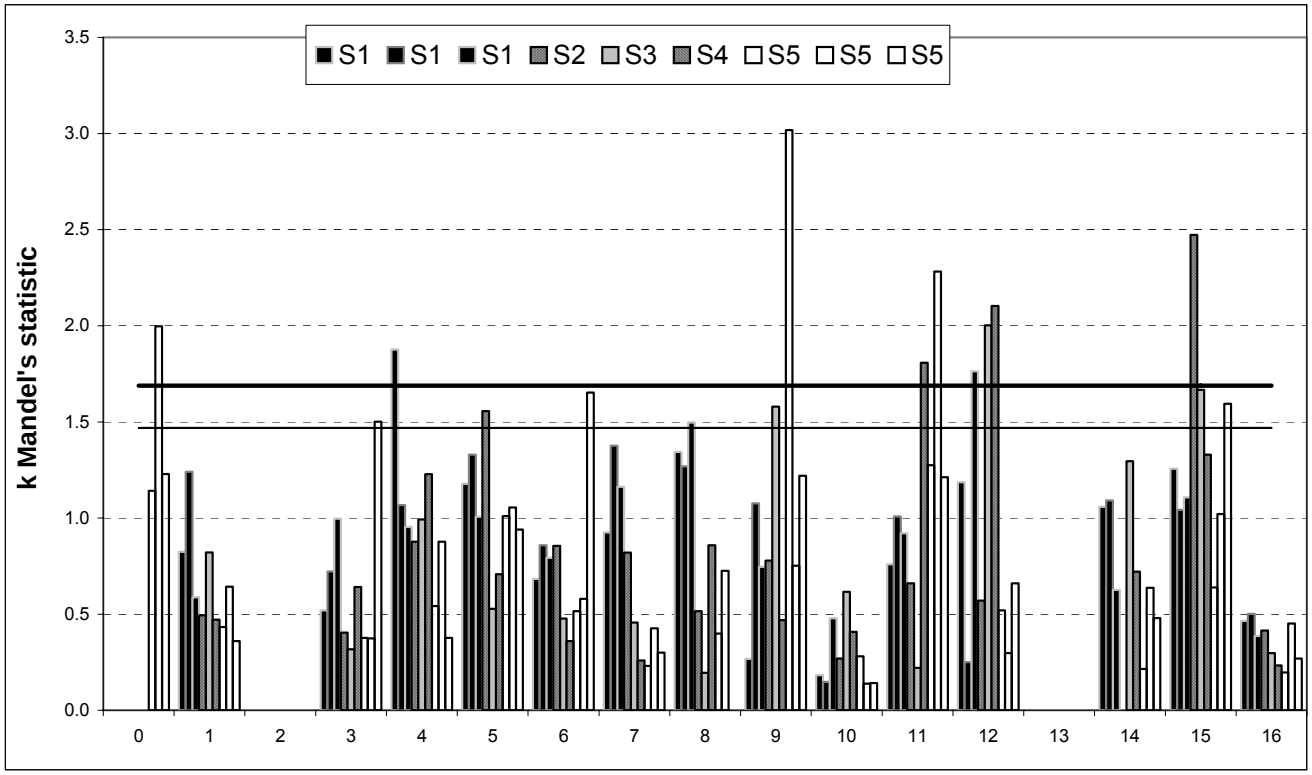



**Figure 32:** Mandel's k statistic for Pb versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The obvious irregularities are cancelled but the figure gives the Mandel's k statistic before any outlier being discarded.

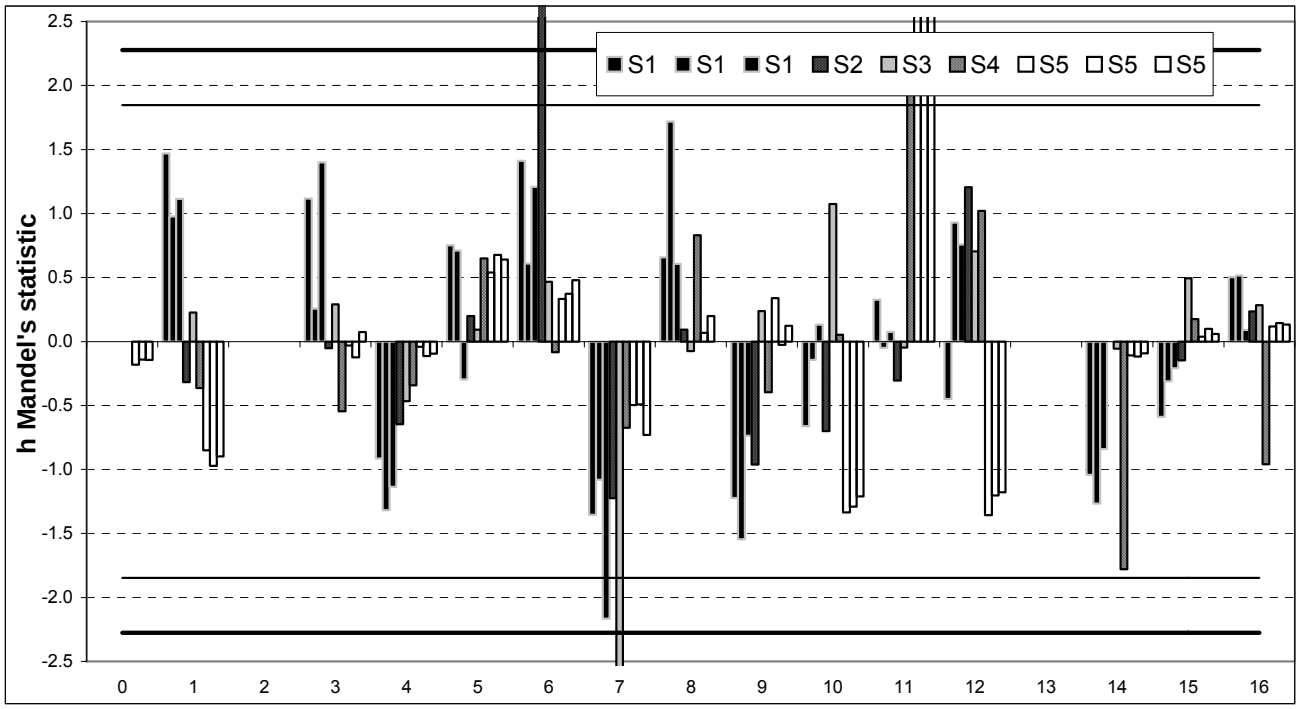



**Figure 33:** Mandel's h statistic for Pb versus laboratories and test-samples.
The bold line shows the critic value for k with 99 % probability while the solid line shows the one with 95 % probability. The figure gives the Mandel's h statistic before any obvious irregularities and statistical outliers were cancelled.

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**Abstract**
The Joint Research Centre (JRC) has carried out an Intercomparison Exercise (IE) for the determination of heavy metals in particulate matter (PM10). The IE focussed on lead (Pb), arsenic (As), nickel (Ni) and cadmium (Cd), the heavy metals regulated by the 1st and 4th Daughter Directives for Air Pollution. Copper (Cu), chromium (Cr) and zinc (Zn), the elements included in the EMEP programme together with aluminium (Al), cobalt (Co), iron (Fe), manganese (Mn) and vanadium (V) were also tested. Fourteen laboratories, generally members of the Network of Air Quality Reference Laboratories (AQUILA), participated in the IE. The participants mainly used microwave digestion with nitric acid and hydrogen peroxide and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) for analysis as recommended in the reference method (EN 14902). However, a few participants used other methods: Energy Dispersive X-ray Fluorescence (EDXRF), Atomic Emission Spectrometry (ICP-AES) and Voltammetry for analysis and vaporisation on hot plate before microwave digestion, Soxhlet extraction, high pressure or cold Hydrogen Fluoride methods for digestion.

Each participant received 5 samples to be analysed: (1) a liquid sample prepared by dilution of a Certified Reference Material (CRM), (2) a solution of a dust CRM sample digested by the JRC, (3) a sub-sample of a dust CRM that each participating laboratory had to digest and analyse, (4) a solution prepared by JRC after digestion of an exposed filter with particulate matter sampled at a urban background site and (5) a pair of filters (one blank filter and one exposed filter) to be digested and analysed by each participant.

For 89 % of all types of samples, the Data Quality Objectives (DQOs) of the 1st and 4th European Directives (uncertainty of 25 % for Pb and 40 % for As, Cd and Ni) were met. All together, this is a very good score. The best results were obtained for the liquid CRM, dust CRM digested by JRC, dust CRM and filter digested by JRC with 92, 90, 96 and 93 % of DQOs being met, respectively. It was found that the DQOs were not met if the difference of acidity between test samples and participant calibration standards was high.

Conversely, only 76 % of DQOs were met for the filter to be digested by each participant (about 85 % for Cd and Ni, 73 % for Pb and 64 for As, the latter element being the most difficult one to determine. The worst results were associated with special events: explosion in microwave oven during digestion for two participants, a wrong dilution factor used by one participant and a huge contamination in the blank filter for another participant. For one of the explosions, the microwave digestion and the digestion program advised by EN 14902 is to be questioned. Moreover, satisfactory results were obtained using other mineralisation methods such as Soxhlet extraction, high pressure method and cold hydrogen fluoride digestion which are not presented in EN 14902.

Regarding the methods of analysis, the DQOs of As and Cd could not be met with EDXRF whose limit of detection was too high for these two elements. For Cd analysis, Voltammetry was found inappropriate as this method suffered a strong interference for this element. Good results were observed using ICP-OES for Cd, Ni and Pb. A few discrepancies were also registered for GF-AAS and ICP-MS that were created by the special events or acidity problem mentioned above.

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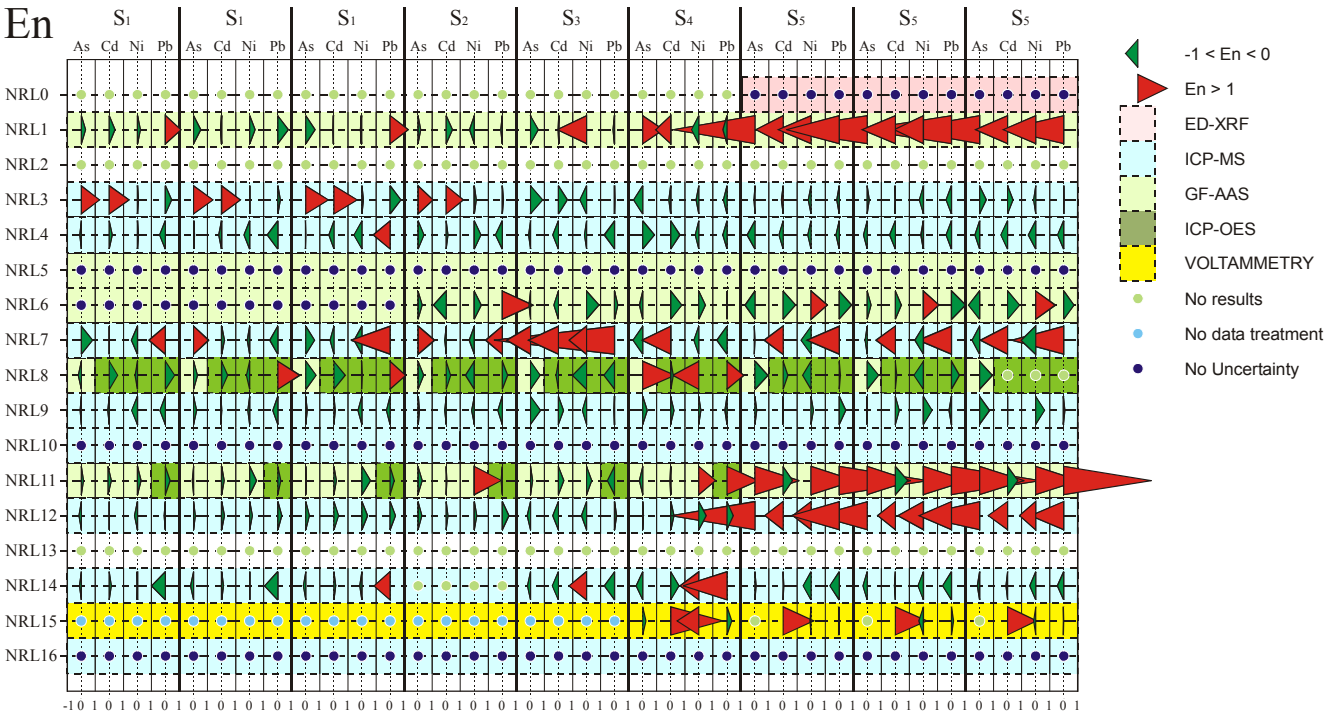


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